

EXHIBIT D

METHOD FOR THE ANALYSIS OF LOW CONCENTRATION WATER FOR  
VOLATILE (PURGEABLE) ORGANIC COMPOUNDS

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# Exhibit D -- Analytical Methods for Volatiles

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1.0 SCOPE AND APPLICATION

- 1.1 The analytical method that follows is designed to analyze water samples containing low concentrations of the volatile compounds listed in the Target Compound List (TCL) in Exhibit C. The majority of the samples are expected to be obtained from drinking water and well/ground water type sources around Superfund sites. The method is based on EPA Method 524.2 and the volatile method contained in the Contract Laboratory Program (CLP) Statement of Work (SOW), "Organic Analysis, Multi-Media, Multi-Concentration". The sample preparation and analysis procedures included in this method are based on purge and trap Gas Chromatograph/Mass Spectrometer (GC/MS) techniques.<sup>1</sup>
- 1.2 Dichlorodifluoromethane, Trichlorofluoromethane, 1,1,2-Trichloro-1,2,2-trifluoroethane, Methyl Acetate, 1,2,3-Trichlorobenzene, Methyl tert-butyl ether, Cyclohexane, Methylcyclohexane, and Isopropylbenzene have been added to the TCL.
- 1.3 Problems that have been associated with the following compounds analyzed by this method include:
- Chloromethane, vinyl chloride, bromomethane, and chloroethane may display peak broadening if the compounds are not delivered to the GC column in a tight band.
  - Acetone, hexanone, 2-butanone, and 4-methyl-2-pentanone have poor purge efficiencies.
  - 1,1,1-Trichloroethane and all of the dichloroethanes may dehydrohalogenate during storage or analysis.
  - Tetrachloroethane and 1,1-dichloroethane may be degraded by contaminated transfer lines in purge and trap systems and/or active sites in trapping materials.
  - Chloromethane may be lost if the purge flow is too fast.
  - Bromoform is one of the compounds most likely to be adversely affected by cold spots and/or active sites in the transfer lines. Response of its quantitation ion (m/z 173) is directly affected by the tuning of 4-Bromofluorobenzene (BFB) at ions m/z 174/176. Increasing the m/z 174/176 ratio within the specified Quality Control (QC) limits may improve bromoform response.
  - Due to the lower quantitation limits required by this method, extra caution must be exercised when identifying compounds.

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<sup>1</sup>This analytical method includes the use of Deuterated Monitoring Compounds (DMC) for precision and accuracy assessment.

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Summary of Method

2.0 SUMMARY OF METHOD

2.1 An inert gas is bubbled through a 25 milliliter (mL) sample contained in a specially designed purging chamber at ambient temperature causing the purgeables to be transferred from the water/aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the purgeables are trapped. After purging is completed, the sorbent column is heated and backflushed with the inert gas to desorb the purgeables onto a Gas Chromatograph (GC) wide-bore capillary column. The GC is temperature programmed to separate the purgeables, which are then detected with a Mass Spectrometer (MS).

2.2 Deuterated Monitoring Compounds (DMCs) and internal standards are added to all samples and blanks. The target compounds and DMCs are identified in the samples and blanks by analyzing standards that contain all target compounds, DMCs, and internal standards under the same conditions and comparing resultant mass spectra and GC retention times. A Relative Response Factor (RRF) is established for each target compound and DMC during the initial and continuing calibrations. The mass spectra response from the Extracted Ion Current Profile (EICP) for the primary quantitation ion produced by that compound is compared to the mass spectra response for the primary quantitation ion produced by the associated internal standard compound. Each identified target compound and DMC is quantitated by comparing the instrument response for the compound in the sample or blank with the instrument response of the associated internal standard, while taking into account the RRF from the most recent mid-point calibration, the sample volume, and any sample dilutions.

2.3 Non-target compounds are identified by comparing the resultant mass spectra from the non-target compounds to mass spectra contained in the NIST/EPA/NIH (May 1992 release or later) and/or Wiley (1991 release or later) or equivalent mass spectral library. Non-target compounds are quantitated by comparing the mass spectra response from the total ion chromatograms to the mass spectra response of the nearest internal standard compound. A RRF of 1 is assumed.

3.0 DEFINITIONS

See Exhibit G for a complete list of definitions.

4.0 INTERFERENCES

- 4.1 Method interference may be caused by impurities in the purge gas, organic compounds out-gassing from the plumbing ahead of the trap, and solvent vapors in the laboratory. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory method and instrument blanks as described in Section 12. The use of non-polytetrafluoroethylene (PTFE) tubing, non-PTFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.
- 4.2 Samples can be contaminated by diffusion of purgeable organics (particularly methylene chloride, fluorocarbons, and other common laboratory solvents) through the septum seal into the sample during storage and handling. Therefore, these samples must be stored separately from other laboratory samples and standards and must be analyzed in a room whose atmosphere is demonstrated to be free of all potential contaminants which will interfere with the analysis.
- 4.3 Contamination by carryover can occur whenever high level and low level samples are sequentially analyzed. To reduce carryover, the purging device and sampling syringe must be rinsed with reagent water between sample analyses. Whenever an unusually concentrated sample is encountered, it must either be followed by analysis of an instrument blank, or the next sample must be closely monitored to check for cross contamination. For samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds, or high purgeable levels, it may be necessary to wash out the purging device with a detergent solution between analyses, rinse it with distilled water, and then dry it in an oven at 105°C. The trap and other parts of the system are also subject to contamination; therefore, frequent bakeout and purging of the entire system may be required.
- 4.4 The laboratory where volatile analysis is performed should be completely free of solvents.

5.0 SAFETY

- 5.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis.
- 5.2 The following analytes covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: benzene; carbon tetrachloride; chloroform; and vinyl chloride. Primary standards of these toxic compounds should be prepared in a hood. A NIOSH/MESA-approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.



6.0 EQUIPMENT AND SUPPLIES

Brand names, suppliers, and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and supplies other than those specified here, but demonstration of equivalent performance meeting the requirements of the Statement of Work (SOW) is the responsibility of the Contractor. The Contractor shall document any use of alternate equipment or supplies in the Sample Delivery Group (SDG) Narrative.

6.1 Glassware

6.1.1 Syringes - 25 milliliters (mL), gas-tight with shut-off valve. Micro syringes - 10 microliters ( $\mu$ L) and larger, 0.006 inch (0.15 mm) ID needle.

6.1.2 Syringe Valve - two-way, with Luer ends (three each), if applicable to the purging device.

6.1.3 Pasteur Pipets - disposable.

6.1.4 Vials and Caps - assorted sizes.

6.1.5 Volumetric Flasks, class A with ground-glass stoppers.

6.1.6 Bottles - 15 mL, screw-cap, with PTFE cap liner.

6.2 pH Paper - wide range

6.3 Balances

Balances must be analytical and capable of accurately weighing  $\pm 0.0001$  g. The balance must be calibrated with class S weights or known reference weights once per each 12-hour work shift. The balance must be calibrated with class S weights at a minimum of once per month. The balance must also be annually checked by a certified technician.

6.4 Purge and Trap Device

The purge and trap device consists of three separate pieces of equipment: the sample purge chamber, trap, and the desorber. Several complete devices are now commercially available.

6.4.1 The sample purge chamber must be designed to accept 25 mL samples with a water column at least 10 centimeters (cm) deep. The gaseous head space between the water column and the trap must have a total volume of less than 15 mL. The purge gas must pass through the water column as finely divided bubbles, each with a diameter of less than 3 millimeters (mm) at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column.

6.4.2 The trap must be at least 25 cm long and have an inside diameter of at least 0.105 inch (2.667 mm). The trap must be packed to contain the following minimum lengths of absorbents: (starting from inlet) 0.5 cm silanized glass wool, 1 cm methyl silicone, 8 cm of 2,6-

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- diphenylene oxide polymer (Tenax-GC, 60/80 mesh), 8 cm of silica gel (Davison Chemical, 35/60 mesh, grade 15 or equivalent), 7 cm of coconut charcoal (prepare from Barnebey Cheney, CA-580-26, or equivalent, by crushing through 26 mesh screen), and 0.5 cm silanized glass wool. A description of the trap used for analysis shall be provided in the SDG Narrative.
- 6.4.3 The desorber must be capable of rapidly heating the trap to 180°C. The polymer section of the trap should not be heated higher than 180°C and the remaining sections should not exceed 220°C during bakeout mode.
- 6.4.4 Trap Packing
- 6.4.4.1 2,6-Diphenylene oxide polymer, 60/80 mesh chromatographic grade (Tenax GC or equivalent).
- 6.4.4.2 Methyl silicone packing, 3.0 percent OV-1 on Chromosorb W, 60/80 mesh (or equivalent).
- 6.4.4.3 Silica gel, 35/60 mesh, Davison, grade 15 (or equivalent).
- 6.4.4.4 Coconut charcoal (prepare from Barnebey Cheney, CA-580-26, or equivalent, by crushing through 26 mesh screen).
- 6.4.4.5 Alternate sorbent traps may be used if:
- The trap packing materials do not introduce contaminants which interfere with identification and quantitation of the compounds listed in Exhibit C (Volatiles);
  - The analytical results generated using the trap meet the initial and continuing calibration technical acceptance criteria listed in the SOW and the Contract Required Quantitation Limits (CRQLs) listed in Exhibit C (Volatiles); or
  - The trap can accept up to 1000 nanograms (ng) of each compound listed in Exhibit C (Volatiles) without becoming overloaded.
- 6.4.4.5.1 The alternate trap must be designed to optimize performance. Follow the manufacturer's instructions for the use of its product. Before use of any trap other than the one specified in Section 6.4.2, the Contractor must first meet the criteria listed in Section 6.4.4.5. Once this has been demonstrated, the Contractor must document its use in each SDG Narrative by specifying the trap composition (packing material/brand name, amount of packing material). Other sorbent traps include, but are not limited to, Tenax/Silica Gel/Carbon Trap from EPA Method 524.2, Tenax - GC/Graphpac-D Trap (Alltech) or equivalent, and Vocarb 4000 Trap (Supelco) or equivalent.
- 6.4.4.5.2 The Contractor must maintain documentation that the alternate trap meets the criteria listed in Section 6.4.4.5. The minimum documentation requirements are as follows:

- 6.4.4.5.2.1 Manufacturer-provided information concerning the performance characteristics of the trap.
- 6.4.4.5.2.2 Reconstructed ion chromatograms and data system reports generated on the Contractor's GC/MS used for CLP analyses:
- From instrument blank analyses which demonstrate that there are no contaminants which interfere with the volatile analysis when using the alternate trap; and
  - From initial and continuing calibration standards analyzed using the trap specified in Section 6.4.4.
- 6.4.4.5.2.3 Based on Contractor-generated data described above, the Contractor must complete a written comparison/review, which has been signed by the Laboratory Manager, certifying that:
- The alternate trap performance meets the technical acceptance criteria listed in Sections 9.3.5 and 9.4.5;
  - The low point initial calibration standard analysis has adequate sensitivity to meet the volatile CRQLs;
  - The high point initial calibration standard analysis was not overloaded; and
  - The alternate trap materials do not introduce contaminants which interfere with the identification and/or quantitation of the compounds listed in Exhibit C (Volatiles).
- 6.4.4.5.2.4 The documentation must be made available to USEPA during on-site laboratory evaluations or sent to USEPA upon request of the USEPA CLP Project Officer (CLP PO) or the Organic Program Manager at the Analytical Operations/Data Quality Center (AOC).
- 6.4.5 The purge and trap apparatus may be assembled as a separate unit or be an integral unit coupled with a Gas Chromatograph (GC).
- 6.5 Gas Chromatograph/Mass Spectrometer (GC/MS) System
- 6.5.1 Gas Chromatograph - The GC system must be capable of temperature programming and have a flow controller that maintains a constant column flow rate throughout desorption and temperature program operations. The system must include or be interfaced to a purge and trap system as specified in Section 6.4 and have all required accessories including syringes, analytical columns, and gases. All GC carrier gas lines must be constructed from stainless steel or copper tubing. Non-polytetrafluoroethylene (PTFE) thread sealants, or flow controllers with rubber components, are not to be used. The column oven must be cooled to 10°C if adequate separation of gaseous compounds is not achieved (Section 9.1.2.3); therefore, a subambient oven controller is required.

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6.5.2 Gas Chromatography Columns

A description of the column used for analysis shall be provided in the SDG Narrative.

- 6.5.2.1 Minimum length 30 m x 0.53 mm ID VOCOL (Supelco) or equivalent fused silica widebore capillary column with 3 micrometers ( $\mu\text{m}$ ) film thickness.
- 6.5.2.2 Minimum length 30 m x 0.53 mm ID DB-624 (J & W Scientific) or equivalent fused silica widebore capillary column with 3  $\mu\text{m}$  film thickness.
- 6.5.2.3 Minimum length 30 m x 0.53 mm ID AT-624 (Alltech) or equivalent fused silica widebore capillary column with 3  $\mu\text{m}$  film thickness.
- 6.5.2.4 Minimum length 30 m x 0.53 mm ID HP-624 (Hewlett-Packard) or equivalent fused silica widebore capillary column with 3  $\mu\text{m}$  film thickness.
- 6.5.2.5 Minimum length 30 m x 0.53 mm ID RTx-624 (Restek) or equivalent fused silica widebore capillary column with 3  $\mu\text{m}$  film thickness.
- 6.5.2.6 Minimum length 30 m x 0.53 mm ID BPX-624 (SGE) or equivalent fused silica widebore capillary column with 3  $\mu\text{m}$  film thickness.
- 6.5.2.7 Minimum length 30 m x 0.53 mm ID CP-Sil 13CB (Chrompack) or equivalent fused silica widebore capillary column with 3  $\mu\text{m}$  film thickness.

6.5.3 A capillary column is considered equivalent if:

- The column does not introduce contaminants which interfere with the identification and quantitation of the compounds listed in Exhibit C (Volatiles);
- The analytical results generated using the column meet the initial and continuing calibration technical acceptance criteria listed in the SOW, and the CRQLs listed in Exhibit C (Volatiles);
- The column can accept up to 1000 ng of each compound listed in Exhibit C (Volatiles) without becoming overloaded; and
- The column provides equal or better resolution of the compounds listed in Exhibit C (Volatiles) than the columns listed in Section 6.5.2.

6.5.3.1 As applicable, follow the manufacturer's instructions for use of its product.

6.5.3.2 The Contractor must maintain documentation that the column met the criteria in Section 6.5.3. The minimum documentation is as follows:

- 6.5.3.2.1 Manufacturer provided information concerning the performance characteristics of the column.
- 6.5.3.2.2 Reconstructed ion chromatograms and data system reports generated on the GC/MS used for the CLP analyses:
- From instrument blanks which demonstrate that there are no contaminants which interfere with the volatile analysis when using the column; and
  - From initial and continuing calibration standards analyzed using the alternate column.
- 6.5.3.5 Based on the Contractor-generated data described above, the Contractor shall complete a written comparison/review, signed by the Laboratory Manager, certifying that:
- The alternate column performance meets the technical acceptance criteria in Sections 9.3.5 and 9.4.5;
  - The low point initial calibration standard analysis has adequate sensitivity to meet the volatile CRQLs;
  - The high point initial calibration standard analysis was not overloaded; and
  - The column does not introduce contaminants which interfere with the identification and/or quantitation of compounds listed in Exhibit C (Volatiles).
- 6.5.3.6 The documentation must be made available to USEPA during on-site laboratory evaluations or sent to USEPA upon request of the CLP PO or the Organic Program Manager at the AOC.
- 6.5.4 **PACKED COLUMNS CANNOT BE USED.**
- 6.5.5 Mass Spectrometer (MS) - The MS must be capable of scanning from 35 to 300 atomic mass unit (amu) every 2 seconds or less, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode and producing a mass spectrum which meets all the 4-Bromo-fluorobenzene (BFB) GC/MS performance check technical acceptance criteria in Table D-1 when 50 ng of BFB are injected through the GC inlet.
- NOTE: To ensure sufficient precision of mass spectral data, the MS scan rate must allow acquisition of at least five spectra while a sample compound elutes from the GC. The purge and trap GC/MS system must be in a room whose atmosphere is demonstrated to be free of all potential contaminants which will interfere with the analysis. The instrument must be vented to outside the facility or to a trapping system which prevents the release of contaminants into the instrument room.
- 6.5.6 GC/MS Interface - Any GC/MS interface may be used that gives acceptable calibration points at 25 ng or less per injection for each

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of the purgeable target compounds and deuterated monitoring compounds and achieves all acceptable performance criteria. GC/MS interfaces constructed of all-glass or glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane.

- 6.5.7 Data System - A computer system must be interfaced to the MS that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching of any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundance in any EICP between specified time or scan number limits. Also, for the non-target compounds, software must be available that allows comparing sample spectra against reference library spectra. The NIST/EPA/NIH (May 1992 release or later) and/or Wiley (1991 release or later) or equivalent mass spectral library shall be used as the reference library. The data system must be capable of flagging all data files that have been edited manually by laboratory personnel.
- 6.5.8 Magnetic Tape Storage Device - Capable of recording data and must be suitable for long-term, off-line storage.

7.0 REAGENTS AND STANDARDS

7.1 Reagents

Reagents shall be dated with the receipt date and used on a first-in, first-out basis. The purity of the reagents shall be verified before use.

7.1.1 Reagent water - Reagent water is defined as water in which no purgeable target compound is observed at or above the Contract Required Quantitation Limit (CRQL) listed in Exhibit C for that compound and in which no non-target compound is observed at or above 2.0 micrograms per liter ( $\mu\text{g/L}$ ).

7.1.1.1 Reagent water may be generated by passing tap water through a carbon filter bed containing about 453 g (1 lb.) of activated carbon (Calgon Corp., Filtrasorb-300, or equivalent).

7.1.1.2 Reagent water may be generated using a water purification system (Millipore Super-Q or equivalent).

7.1.1.3 Reagent water may be prepared by boiling water for 15 minutes. Subsequently, while maintaining the temperature at 90°C, bubble a contaminant-free inert gas through the water for one hour. While still hot, transfer the water to a narrow-mouth screw-cap bottle, seal with a PTFE-lined septum, and cap.

7.1.2 Methanol - HPLC quality or equivalent -- Each lot of methanol used for analysis under this contract must be purged with nitrogen and must be demonstrated to be free of contaminants that interfere with the measurement of purgeable compounds listed in Exhibit C.

7.2 Standards

The Contractor must provide all standards to be used with this contract. These standards may be used only after they have been certified according to the procedure in Exhibit E. The Contractor must be able to verify that the standards are certified. Manufacturer's certificates of analysis must be retained by the Contractor and presented upon request.

7.2.1 Stock Standard Solutions

Stock standard solutions may be purchased or may be prepared in methanol from pure standard materials.

7.2.1.1 Prepare stock standard solutions by placing about 9.8 milliliters (mL) of methanol into a 10.0 mL ground-glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 minutes or until all alcohol wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

7.2.1.2 Add the assayed reference material as described below.

7.2.1.2.1 If the compound is a liquid, use a 100 microliters ( $\mu\text{L}$ ) syringe to immediately add two or more drops of assayed reference

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Reagents and Standard (Con't)

material to the flask, then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

7.2.1.2.2 If the compound is a gas at room temperature, fill a 5 mL valved gas-tight syringe with the reference standard to the 5.0 mL mark. Lower the needle to 5 millimeters (mm) above the methanol meniscus. Slowly introduce the reference standard above the surface of the liquid. The gas will rapidly dissolve in the methanol. This may also be accomplished by using a lecture bottle equipped with a Hamilton Lecture Bottle Septum (#86600). Attach PTFE tubing to the side-arm relief valve and direct a gentle stream of the reference standard into the methanol meniscus.

7.2.1.3 Reweigh, dilute to volume, stopper, then mix by inverting the flask several times. For non-gaseous compounds, calculate the concentration in  $\mu\text{g}/\mu\text{L}$  from the net gain in weight. When compound purity is assayed to be 97 percent or greater, the weight may be used without correction to calculate the concentration of the stock standard. If the compound purity is assayed to be less than 97 percent, the weight must be corrected when calculating the concentration of the stock solution. For gaseous compounds, calculate the concentration in  $\mu\text{g}/\mu\text{L}$  using the Ideal Gas Law, taking into account the temperature and pressure conditions within the laboratory.

7.2.1.4 Prepare fresh stock standards every two months for gases or for reactive compounds such as styrene. All other stock standards for non-gases/non-reactive purgeable compounds must be replaced after six months, or sooner if standard has degraded or evaporated.

7.2.2 Secondary Dilution Standards

7.2.2.1 Using stock standard solutions, prepare secondary dilution standards in methanol that contain the compounds of interest, either singly or mixed together. Secondary dilution standard solutions should be prepared at concentrations that can be easily diluted to prepare working standard solutions.

7.2.2.2 Prepare fresh secondary dilution standards for gases and for reactive compounds, such as styrene, every month or sooner if standard has degraded or evaporated. Secondary dilution standards for the other purgeable compounds must be replaced after six months, or sooner if standard has degraded or evaporated.

7.2.3 Working Standards

7.2.3.1 Instrument Performance Check Solution (4-Bromofluorobenzene)

Prepare a 25 nanograms per microliter ( $\text{ng}/\mu\text{L}$ ) solution of 4-Bromofluorobenzene (BFB) in methanol. Prepare fresh BFB solution every six months, or sooner if the solution has degraded or evaporated.



NOTE: The 25 ng/μL concentration is used with a 2 μL injection volume. The laboratory may prepare a 50 ng/μL solution of BFB if a 1 μL injection volume is used.

#### 7.2.3.2 Calibration Standard Solution

Prepare the working calibration standard solution containing all of the purgeable target compounds in methanol (Exhibit C). The concentration of the non-ketone target compounds and the associated Deuterated Monitoring Compounds (DMCs) must be 2.5 μg/mL in the standard (i.e., final concentration). The concentration of the ketones (acetone, butanone, 2-hexanone, 4-methyl-2-pentanone) and their associated DMCs must be 12.5 μg/mL in the standard (i.e., final concentration). Prepare fresh working calibration standard solutions weekly, or sooner if solutions have degraded or evaporated.

#### 7.2.3.3 Internal Standard Spiking Solution

Prepare an internal standard spiking solution containing 1,4-dichlorobenzene-d<sub>4</sub>, chlorobenzene-d<sub>5</sub>, and 1,4-difluorobenzene in methanol at the concentration of 12.5 μg/mL for each internal standard. Add 10 μL of this spiking solution into 25.0 mL of samples, blanks, requested Matrix Spike/Matrix Spike Duplicate(s) (MS/MSD), and calibration standards for a concentration of 5.0 μg/L. Prepare fresh spiking solution weekly, or sooner if the solution has degraded or evaporated.

#### 7.2.3.4 Deuterated Monitoring Compound (DMC) Spiking Solution

Prepare a DMC spiking solution in methanol containing the compounds listed below at the following concentrations:

<u>Compound</u>	<u>Concentration</u> <u>μg/mL</u>
Vinyl Chloride-d <sub>3</sub>	12.5
Chloroethane-d <sub>5</sub>	12.5
1,1-Dichloroethene-d <sub>2</sub>	12.5
2-Butanone-d <sub>5</sub>	12.5
Chloroform-d	12.5
1,2-Dichloroethane-d <sub>4</sub>	12.5
Benzene-d <sub>6</sub>	12.5
1,2-Dichloropropane-d <sub>6</sub>	12.5
Toluene-d <sub>8</sub>	12.5
trans-1,3-Dichloropropene-d <sub>4</sub>	12.5
2-Hexanone-d <sub>5</sub>	12.5
Bromoform-d	12.5
1,1,2,2-Tetrachloroethane-d <sub>2</sub>	12.5
1,2-Dichlorobenzene-d <sub>4</sub>	12.5

Add 10 μL of this spiking solution into 25 mL of sample, and blank for a concentration of 5.0 μg/L. The DMC spiking solution is added to the working calibration standards so it is not to be added again when aqueous calibration standards are prepared.

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Prepare fresh spiking solution weekly, or sooner if the solution has degraded or evaporated.

7.2.3.5 Matrix Spiking Solution

Prepare a spiking solution in methanol that contains the following compounds at a concentration of 12.5 µg/mL; 1,1-Dichloroethene, Trichloroethene, Chlorobenzene, Toluene, and Benzene. Prepare fresh spiking solution weekly, or sooner, if the solution has degraded or evaporated.

7.2.3.6 Aqueous Calibration Standard Solutions -- Initial and Continuing

7.2.3.6.1 Prepare five aqueous initial calibration standard solutions containing all of the purgeable target compounds and the DMCs at the following levels: all non-ketone target compounds and non-ketone DMCs at 0.50, 1.0, 5.0, 10, and 25 µg/L; all ketones and their associated DMCs at 5.0, 10, 25, 50 and 125 µg/L. It is required that all three xylene isomers (o-, p-, and m-xylene) be present in the calibration standards at concentrations of each isomer equal to that of the other target compounds (i.e., 0.50, 1.0, 5.0, 10, and 25 µg/L). The internal standards are added to each calibration standard according to the procedure in Section 9.3.3.4.

7.2.3.6.2 Aqueous calibration standards may be prepared in a volumetric flask or in the syringe used to inject the standard into the purging device.

7.2.3.6.2.1 Volumetric flask - Add an appropriate volume of working calibration standard solution to an aliquot of reagent water in a volumetric flask. Use a microsyringe and rapidly inject the alcohol standard into the expanded area of the filled volumetric flask. Remove the needle as quickly as possible after injection. Bring to volume. Mix by inverting the flask three times only. Discard the contents contained in the head of the flask.

7.2.3.6.2.2 Syringe - Remove the plunger from a 25 mL syringe and close the syringe valve. Pour reagent water into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the water. Invert the syringe, open the syringe valve, and vent any residual air. Adjust the water volume to 25.0 mL minus the amount of calibration standard to be added. Withdraw the plunger slightly and add an appropriate volume of working calibration standard through the valve bore of the syringe. Close the valve and invert three times.

7.2.3.6.3 The 5.0 µg/L (25 µg/L for ketones) aqueous calibration standard solution is the continuing calibration standard.

7.2.3.6.4 The methanol contained in each of the aqueous calibration standards must not exceed 1 percent by volume.

7.2.4 Ampulated Standard Extracts

Standard solutions purchased from a chemical supply house as ampulated extracts in glass vials may be retained and used until the expiration date provided by the manufacturer. If no manufacturer's expiration date is provided, the standard solutions as ampulated extracts may be retained and used for 2 years from the preparation date. Standard solutions prepared by the Contractor which are immediately ampulated in glass vials may be retained for 2 years from preparation date. Upon breaking the glass seal, the expiration times listed in Sections 7.2.1 to 7.2.3 will apply. The Contractor is responsible for assuring that the integrity of the standards has not degraded (Section 7.2.5.5).

7.2.5 Storage of Standards

- 7.2.5.1 Store the stock standards in PTFE-sealed screw-cap bottles with zero headspace at  $-10^{\circ}\text{C}$  to  $-20^{\circ}\text{C}$ , and protect the standards from light. Once one of the bottles containing the stock standard solution has been opened, it may be used for no longer than one week.
- 7.2.5.2 Store secondary dilution standards in PTFE-sealed screw-cap bottles with minimal headspace at  $-10^{\circ}\text{C}$  to  $-20^{\circ}\text{C}$ . Protect the standards from light. The secondary dilution standards must be checked frequently for signs of degradation or evaporation, especially just prior to preparing the working calibration standards from them.
- 7.2.5.3 Aqueous standards may be stored up to 24 hours if held in PTFE-sealed screw-cap vials with zero headspace at  $4^{\circ}\text{C}$  ( $\pm 2^{\circ}\text{C}$ ), and protect the standards from light. If not so stored, they must be discarded after one hour unless they are set up to be purged by an autosampler. When using an autosampler, the standards may be kept up to 12 hours in purge tubes connected via the autosampler to the purge and trap device.
- 7.2.5.4 Purgeable standards must be stored separately from other standards.
- 7.2.5.5 The Contractor is responsible for maintaining the integrity of standard solutions and verifying prior to use. This means that standards must be brought to room temperature prior to use, checked for losses, and checked that all components have remained in the solution.

7.2.6 Temperature Records for Storage of Standards

- 7.2.6.1 The temperature of all standard storage refrigerators/freezers shall be recorded daily.
- 7.2.6.2 Temperature excursions shall be noted and appropriate corrective actions shall be taken to correct problems, when required.

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Sample Collection, Preservation, and Storage

7.2.6.3 Corrective action Standard Operating Procedures (SOPs) shall be posted on the refrigerators.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Sample Collection and Preservation

8.1.1 Water samples may be collected in glass containers having a total volume of at least 40 milliliters (mL) with a PTFE-lined septum and an open top screw-cap. Headspace should be avoided. The specific requirements for site sample collection are outlined by the Region.

8.1.2 The containers must be filled in such a manner that no air bubbles pass through the sample as the container is being filled. Seal the vial so that no air bubbles are entrapped in it.

8.1.3 Water samples are preserved to a pH of 2 at the time of collection.

8.1.4 All samples must be iced or refrigerated at 4°C (±2°C) from the time of collection until analysis.

8.2 Procedure for Sample Storage

8.2.1 The samples must be protected from light and refrigerated at 4°C (±2°C) from the time of receipt until 60 days after delivery of a reconciled, complete sample data package to USEPA. After 60 days, the samples may be disposed of in a manner that complies with all applicable regulations.

8.2.2 The samples must be stored in an atmosphere demonstrated to be free of all potential contaminants and in a refrigerator used only for storage of volatile samples received under this contract.

8.2.3 All volatile samples in an SDG must be stored together in the same refrigerator.

8.2.4 Storage blanks shall be stored with samples until all samples within an SDG are analyzed.

8.2.5 Samples, sample extracts, and standards must be stored separately.

8.2.6 Volatile standards must be stored separately from semivolatile and pesticide/Aroclor standards.

8.3 Temperature Records for Sample Storage

8.3.1 The temperature of all sample storage refrigerators shall be recorded daily.

8.3.2 Temperature excursions shall be noted and appropriate corrective actions shall be taken to correct problems, when required.

8.3.3 Corrective action Standard Operating Procedures (SOPs) shall be posted on the refrigerators.

#### 8.4 Contract Required Holding Times

Analysis of water samples must be completed within 10 days of Validated Time of Sample Receipt (VTSR). As part of USEPA's Quality Assurance (QA) program, USEPA may provide Performance Evaluation (PE) Samples as standard extracts which the Contractor is required to prepare per the instructions provided by USEPA. PE samples must be prepared and analyzed concurrently with the samples in the SDG. The contract-required 10-day holding time does not apply to PE Samples received as standard extracts.

#### 9.0 CALIBRATION AND STANDARDIZATION

##### 9.1 Instrument Operating Conditions

###### 9.1.1 Purge and Trap

- 9.1.1.1 The following are the recommended purge and trap analytical conditions. The conditions are recommended unless otherwise noted:

###### Purge Conditions

Purge Gas:	Helium or Nitrogen
Purge Time:	11.0 ±0.1 minute
Purge Flow Rate:	25-40 mL/minute
Purge Temperature:	Ambient temperature (required)

###### Desorb Conditions

Desorb Temperature:	180°C
Desorb Flow Rate:	15 mL/minute
Desorb Time:	4.0 ±0.1 minute

###### Trap Reconditioning Conditions

Reconditioning Temperature:	180°C
Reconditioning Time:	7.0 ±0.1 minute (minimum). A longer time may be required to bake contamination or water from the system.

- 9.1.1.2 Before initial use, condition the trap overnight at 180°C by backflushing with at least 20 milliliters (mL)/minute flow of inert gas. Do not vent the trap effluent onto the analytical column. Prior to daily use, condition the trap by heating at 180°C for 10 minutes while backflushing. The trap may be vented to the analytical column during daily conditioning; however, the column must be run through the temperature program prior to the analysis of samples and blanks.

- 9.1.1.3 Optimize purge and trap conditions for sensitivity and to minimize cross-contamination between samples. Once optimized, the same

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purge and trap conditions must be used for the analysis of all standards, samples, and blanks.

9.1.1.4 A moisture reduction/water management system may be used to improve the chromatographic performance by controlling moisture or water if:

- The system does not introduce contaminants which interfere with identification and quantitation of compounds listed in Exhibit C (Volatiles),
- The analytical results generated when using the moisture reduction/water management system meet the initial and continuing calibration technical acceptance criteria listed in the Statement of Work (SOW) and the Contract Required Quantitation Limits (CRQLs) listed in Exhibit C (Volatiles);
- All calibration standards, samples, and blanks are analyzed under the same conditions; and
- The Contractor performs acceptably on the Performance Evaluation Samples using this system.

9.1.2 Gas Chromatograph (GC)

9.1.2.1 The following are the recommended GC analytical conditions. The conditions are recommended unless otherwise noted:

Capillary Columns

Carrier Gas:	Helium
Flow Rate:	15 mL/minute
Initial Temperature:	10°C
Initial Hold Time:	1.0 - 5.0 (±0.1) minutes
Ramp Rate:	6°C/minute
Final Temperature:	160°C
Final Hold Time:	Until three minutes after all compounds listed in Exhibit C (Volatiles) elute (required)

9.1.2.2 Optimize GC conditions for analyte separation and sensitivity. Once optimized, the same GC conditions must be used for the analysis of all standards, samples, and blanks.

9.1.2.3 If the gaseous compounds chloromethane, bromomethane, vinyl chloride, and chloroethane fail to exhibit narrow, symmetrical peak shape, are not separated from the solvent front, or are not resolved greater than 90.0 percent from each other, then a subambient oven controller must be used, and the initial temperature must be less than or equal to 10°C.

9.1.3 Mass Spectrometer (MS)

The following are the required MS analytical conditions:

Electron Energy:	70 volts (nominal)
Mass Range:	35-300 amu
Ionization Mode:	EI
Scan Time:	To give at least five scans per peak, not to exceed 2 seconds per scan for capillary column.

9.2 Instrument Performance Check -- 4-Bromofluorobenzene (BFB)

9.2.1 Summary of Instrument Performance Check

9.2.1.1 The GC/MS system must be tuned to meet the manufacturer's specifications, using a suitable calibrant such as perfluoro-tri-n-butylamine (FC-43) or perfluorokerosene (PFK). The mass calibration and resolution of the GC/MS system are verified by the analysis of the instrument performance check solution (Section 7.2.3.1).

9.2.1.2 Prior to the analysis of any samples, blanks, or calibration standards, the Contractor must establish that the GC/MS system meets the mass spectral ion abundance criteria for the instrument performance check solution containing BFB.

9.2.2 Frequency of Instrument Performance Check

The instrument performance check solution must be injected once at the beginning of each 12-hour period, during which samples, blanks or standards are to be analyzed. The 12-hour time period for GC/MS performance check, calibration standards (initial or continuing calibration), blank, and sample analysis begins at the moment of injection of the BFB analysis that the laboratory submits as documentation of a compliant instrument performance check. The time period ends after 12 hours have elapsed according to the system clock.

9.2.3 Procedure for Instrument Performance Check

The analysis of the instrument performance check solution may be performed as follows:

- As an injection of up to 50 nanograms (ng) of BFB into the GC/MS (Section 7.2.3.1); or
- By adding 50 ng of BFB to a calibration standard (Section 7.2.3.2) and analyzing the calibration standard.

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9.2.4 Technical Acceptance Criteria for Instrument Performance Check

- 9.2.4.1 The mass spectrum of BFB must be acquired in the following manner. Three scans (the peak apex scan and the scan immediately preceding and the scan immediately following the apex) are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan no more than 20 scans prior to the beginning of the elution of BFB. Do not background subtract part of the BFB peak.

NOTE: All subsequent standards, samples, and blanks associated with a BFB analysis must use identical MS instrument conditions.

- 9.2.4.2 The analysis of the instrument performance check solution must meet the ion abundance criteria given in Table D-1.

9.2.5 Corrective Action for Instrument Performance Check

- 9.2.5.1 If the BFB technical acceptance criteria are not met, retune the GC/MS system. It may also be necessary to clean the ion source, clean the quadrupole rods, or take other corrective actions to achieve the technical acceptance criteria.
- 9.2.5.2 BFB technical acceptance criteria **must** be met before any standards, samples, or required blanks are analyzed. Any samples or required blanks analyzed when tuning technical acceptance criteria have not been met will require re-analysis at no additional cost to USEPA.

9.3 Initial Calibration

9.3.1 Summary of Initial Calibration

Prior to the analysis of samples and required blanks and after the instrument performance check technical acceptance criteria have been met, each GC/MS system must be calibrated at a minimum of five concentrations to determine instrument sensitivity and the linearity of GC/MS response for the purgeable target and Deuterated Monitoring Compounds (DMCs).

9.3.2 Frequency of Initial Calibration

- 9.3.2.1 Each GC/MS system must be calibrated upon award of the contract, whenever the Contractor takes corrective action which may change or affect the initial calibration criteria (i.e., ion source cleaning or repair, column replacement, etc.), or if the continuing calibration technical acceptance criteria have not been met.
- 9.3.2.2 If time remains in the 12-hour time period after meeting the technical acceptance criteria for the initial calibration, samples and blanks may be analyzed. It is not necessary to analyze a continuing calibration standard if the initial calibration standard that is the same concentration as the continuing calibration standard meets the continuing calibration technical



acceptance criteria. A method blank is required. Quantitate all samples and blank results against the initial calibration standard that is the same concentration as the continuing calibration standard. Compare Quality Control (QC) criteria such as internal standard area response change and retention time shift to the initial calibration standard that is the same concentration as the continuing calibration standard.

9.3.3 Procedure for Initial Calibration

- 9.3.3.1 Assemble a purge and trap device that meets the specifications in Section 6.4. Condition the device as described in Section 9.1.1.
- 9.3.3.2 Connect the purge and trap device to the GC. The GC must be operated using temperature and flow rate parameters equivalent to those in Section 9.1.2.
- 9.3.3.3 All samples, blanks, and standard/spiking solutions must be allowed to warm to ambient temperature (approximately 1 hour) before analysis.
- 9.3.3.4 Add 10 microliters ( $\mu\text{L}$ ) of the internal standard solution (Section 7.2.3.3) to each aqueous standard containing the DMCs for a concentration of 5 micrograms per liter ( $\mu\text{g/L}$ ) at time of purge. Analyze each calibration standard according to Section 10.2.

9.3.4 Calculations for Initial Calibration

Calculating the Relative Response Factor (RRF) of the xylenes requires special attention. On capillary columns, the *m*- and *p*-xylene isomers coelute. Therefore, when calculating the relative response factor in the equation below, use the area response ( $A_x$ ) and concentration ( $C_x$ ) of the peak from *o*-xylene.

- 9.3.4.1 Calculate RRF for each purgeable target compound and DMC using Equation 1. See Table D-3 to associate purgeable target compounds and DMCs with the proper internal standard. See Table D-4 for primary quantitation ions to be used for each purgeable target compound, DMC, and internal standard compound.

NOTE: Unless otherwise stated the area response is that of the primary quantitation ion.

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EQ. 1

$$RRF = \frac{A_x}{A_{is}} \times \frac{C_{is}}{C_x}$$

Where:

$A_x$  = Area of the characteristic ion (EICP) for the compound to be measured (Table D-4).

$A_{is}$  = Area of the characteristic ion (EICP) for the specific internal standard (Tables D-3 and D-4).

$C_{is}$  = Concentration of the internal standard.

$C_x$  = Concentration of the compound to be measured.

\$\$\$

9.3.4.2 The mean Relative Response Factor (RRF) must be calculated for all compounds.

9.3.4.3 Calculate the Percent Relative Standard Deviation (%RSD) of RRF values for each purgeable target and DMC over the initial calibration range using Equation 2 in conjunction with Equation 3.

EQ. 2

$$\%RSD = \frac{SD_{RRF}}{\bar{X}} \times 100$$

Where:

$SD_{RRF}$  = Standard deviation of initial calibration relative response factors (per compound). From EQ. 3.

$\bar{X}$  = Mean value of the initial calibration relative response factors (per compound).

9.3.4.4 Equation 3 is the general formula for Standard Deviation (SD) for a statistically small set of values.

EQ. 3

$$SD = \sqrt{\frac{\sum_{i=1}^n (x_i - \bar{X})^2}{n - 1}}$$

Where:

$x_i$  = Each individual value used to calculate the mean.

$\bar{X}$  = The mean of n values.

n = Total number of values.

9.3.4.5 Equation 4 is the general formula for the mean of a set of values.

EQ. 4

$$\bar{x} = \frac{\sum_{i=1}^n x_i}{n}$$

Where:

$x_i$  = Value.

$\bar{x}$  = Mean value.

$n$  = Number of values.

#### 9.3.5 Technical Acceptance Criteria For Initial Calibration

9.3.5.1 All initial calibration standards must be analyzed at the concentration levels described in Section 7.2.3.6.1, and at the frequency described in Section 9.3.2 on a GC/MS system meeting the BFB technical acceptance criteria (Section 9.2.4).

9.3.5.2 Excluding those ions in the solvent front, no quantitation ion may saturate the detector. Consult the instrument manufacturer's instrument operating manual to determine how saturation is indicated for your instrument.

9.3.5.3 The RRF at each calibration concentration for each purgeable target and DMC that has a required minimum relative response factor value must be greater than or equal to the compound's minimum acceptable relative response factor listed in Table D-2.

9.3.5.4 The %RSD for each target or DMC listed in Table D-2 must be less than or equal to that value listed.

9.3.5.5 Up to two compounds may fail the criteria listed in Sections 9.3.5.3 and 9.3.5.4 and still meet the minimum RRF and %RSD requirements. However, these compounds must have a minimum RRF greater than or equal to 0.010, and the %RSD must be less than or equal to 40.0 percent.

#### 9.3.6 Corrective Action for Initial Calibration

9.3.6.1 If the initial calibration technical acceptance criteria are not met, inspect the system for problems. It may be necessary to clean the ion source, change the column, service the purge and trap device, or take other corrective actions to achieve the technical acceptance criteria.

9.3.6.2 Initial calibration technical acceptance criteria **MUST** be met before any samples or required blanks are analyzed. Any samples

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or required blanks analyzed when initial calibration technical acceptance criteria have not been met will require re-analysis at no additional cost to USEPA.

9.4 Continuing Calibration

9.4.1 Summary of Continuing Calibration

Prior to the analysis of samples and required blanks and after BFB and initial calibration technical acceptance criteria have been met, each GC/MS system must be routinely checked by analyzing a continuing calibration standard containing all the purgeable target and DMCs and internal standards to ensure that the instrument continues to meet the instrument sensitivity and linearity requirements of the SOW.

9.4.2 Frequency of Continuing Calibration

9.4.2.1 A check of the calibration curve must be performed once per every 12-hour time period of operation. The 12-hour time period begins with the injection of BFB.

9.4.2.2 If time remains in the 12-hour time period after meeting the technical acceptance criteria for the initial calibration, samples and blanks may be analyzed. It is not necessary to analyze a continuing calibration standard, if the initial calibration standard that is the same concentration as the continuing calibration standard meets the continuing calibration technical acceptance criteria. A method blank is required. Quantitate all sample and blank results against the initial calibration standard that is the same concentration as the continuing calibration standard (5.0 µg/L for non-ketones, 25 µg/L for ketones).

If time does not remain in the 12-hour period beginning with the injection of the instrument performance check solution, a new injection of the instrument performance check solution must be made. If the new injection meets the ion abundance criteria for BFB, then a continuing calibration standard may be injected.

9.4.3 Procedure for Continuing Calibration

9.4.3.1 Set up the purge and trap GC/MS system per the requirements in Section 9.1.

9.4.3.2 All samples, required blanks, and standard/spiking solutions must be allowed to warm to ambient temperature (approximately 1 hour) before analysis.

9.4.3.3 Add 10 µL of internal standard spiking solution (prepared as described in Section 7.2.3.3 to the 25 mL syringe or volumetric flask containing the continuing calibration standard in Section 7.2.3.6.3). Analyze the continuing calibration standard, according to Section 10.2.

9.4.4 Calculations for Continuing Calibration

9.4.4.1 Calculate a RRF for each target and DMC according to Section 9.3.4.1.

9.4.4.2 Calculate the percent difference between the continuing calibration RRF and the most recent initial calibration mean RRF for each purgeable target and DMC using Equation 5.

EQ. 5

$$\text{Difference} = \frac{\text{RRF}_c - \overline{\text{RRF}_i}}{\overline{\text{RRF}_i}} \times 100$$

Where:

$\text{RRF}_c$  = Relative response factor from current continuing calibration standard.

$\overline{\text{RRF}_i}$  = Mean relative response factor from the most recent initial calibration.

9.4.5 Technical Acceptance Criteria for Continuing Calibration

9.4.5.1 The concentration of the volatile organic target and deuterated monitoring compounds in the continuing calibration standard must be 5.0 µg/L for non-ketones and 25 µg/L for ketones. The continuing calibration standard must be analyzed at the frequency described in Section 9.4.2 on a GC/MS system meeting the BFB (Section 9.2.4) and the initial calibration (Section 9.3.5) technical acceptance criteria.

9.4.5.2 The RRF for each purgeable target and DMC that has a required minimum RRF value must be greater than or equal to the compound's minimum acceptable RRF listed in Table D-2.

9.4.5.3 The RRF percent difference for each purgeable target and DMC listed in Table D-2 must be less than or equal to that value listed.

9.4.5.4 Up to two compounds may fail the requirements listed in Sections 9.4.5.2 and 9.4.5.3 and still meet the minimum RRF criteria and percent difference criteria. However, these compounds must have a minimum RRF greater than or equal to 0.010 and the percent difference must be within the inclusive range of ±40.0 percent.

9.4.5.5 Excluding those ions in the solvent front, no quantitation ion may saturate the detector. Consult the manufacturer's instrument operating manual to determine how saturation is indicated for your instrument.

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9.4.6 Corrective Action for Continuing Calibration

- 9.4.6.1 If the continuing calibration technical acceptance criteria are not met, recalibrate the GC/MS instrument according to Section 9.3. It may be necessary to clean the ion source, change the column, or take other corrective actions to achieve the continuing calibration technical acceptance criteria.
- 9.4.6.2 Continuing calibration technical acceptance criteria MUST be met before any samples or required blanks are analyzed. Any samples or required blanks analyzed when continuing calibration technical acceptance criteria have not been met will require re-analysis at no additional cost to USEPA.

## 10.0 SAMPLE ANALYSIS

### 10.1 Summary of Sample Analysis

- 10.1.1 This method is designed for analysis of samples that contain low concentrations of the target compounds listed in Exhibit C. It is expected that the samples will come from drinking water and well/ground water type sources around Superfund sites. If, upon inspection of a sample, the Contractor suspects that the sample is not amenable to this method, contact Sample Management Office (SMO). SMO will contact the Region for instructions.
- 10.1.2 Prior to the analysis of samples, establish the appropriate purge and trap Gas Chromatograph/Mass Spectrometer (GC/MS) operating conditions, as outlined in Section 9.1, analyze the instrument performance check solution (Section 9.2), and calibrate the GC/MS system according to Sections 9.3 through 9.4.6. Also prior to sample analysis, a method blank must be analyzed that meets blank technical acceptance criteria in Section 12.1.5. All samples, required blanks, and standard/spiking solutions must be allowed to warm to ambient temperature (approximately 1 hour) before analysis. All samples, required blanks, and calibration standards must be analyzed under the same instrument conditions.
- 10.1.3 If insufficient sample volume (less than 90 percent of the required amount) is received to perform the analyses, the Contractor shall contact SMO to apprise them of the problem. SMO will contact the Region for instructions. The Region will either require that no sample analyses be performed or will require a reduced volume be used for the sample analysis. No other changes in the analyses will be permitted. The Contractor shall document the Region's decision in the Sample Delivery Group (SDG) Narrative.

### 10.2 Procedure for Sample Analysis

- 10.2.1 Remove the plunger from a 25 milliliters (mL) syringe that has a closed syringe valve attached. Open the sample or standard container which has been allowed to come to ambient temperature, and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Invert the syringe, open the syringe valve, and vent any residual air while adjusting the sample volume to 25.0 mL. This process of taking an aliquot destroys the validity of the sample for future analysis, unless the excess sample is immediately transferred to a smaller vial with zero headspace and stored at 4°C (±2°C).
- 10.2.2 Once the sample aliquots have been taken from the VOA vial, the pH of the water sample must be determined. The purpose of the pH determination is to ensure that all VOA samples were acidified in the field. Test the pH by placing one or two drops of sample on the pH paper (do not add pH paper to the vial). Record the pH of each sample and report these data in the SDG Narrative, following the instructions in Exhibit B. No pH adjustment is to be performed by the Contractor.

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Add 10.0 microliters ( $\mu\text{L}$ ) of the internal standard spiking solution and 10.0  $\mu\text{L}$  of the Deuterated Monitoring Compound (DMC) standard solution through the valve bore of the syringe, then close the valve. Invert the syringe three times.

10.2.3 Attach the valve assembly on the syringe to the valve on the sample purger. Open the valves and inject the sample into the purging chamber.

10.2.4 Close both valves and purge the sample for 11.0 ( $\pm 0.1$ ) minutes at ambient temperature.

10.2.5 Sample Desorption - After the 11-minute purge, attach the trap to the GC, adjust the purge and trap system to the desorb mode, initiate the temperature program sequence of the GC and start data acquisition. Introduce the trapped material to the GC column by rapidly heating the trap to  $180^{\circ}\text{C}$  while backflushing the trap with inert gas at 15 mL/min for  $4.0 \pm 0.1$  min. While the trapped material is being introduced into the GC, empty the sample purger and rinse it with reagent water. For samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds, or high purgeable levels, it may be necessary to wash out the sample purger with a detergent solution, rinse it with reagent water, and then dry it in an oven at  $105^{\circ}\text{C}$ .

10.2.6 Trap Reconditioning - After desorbing the sample, recondition the trap for a minimum of  $7.0 \pm 0.1$  min at  $180^{\circ}\text{C}$  by returning the purge and trap system to purge mode.

10.2.7 Gas Chromatography - Hold the column temperature at  $10^{\circ}\text{C}$  for 1.0 to 5.0 min, then program at  $6^{\circ}\text{C}/\text{min}$  to  $160^{\circ}\text{C}$  and hold until three minutes after all target volatile compounds have eluted.

NOTE: Once an initial hold time has been chosen and the GC operating conditions optimized, the same GC condition must be used for the analysis.

10.2.8 Termination of Data Acquisition - Three minutes after all the purgeable target compounds have eluted from the GC, terminate the MS data acquisition and store data files on the data system storage device. Use appropriate data output software to display full range mass spectra and appropriate Extracted Ion Current Profiles (EICPs).

10.2.9 Dilutions

10.2.9.1 An original undiluted analysis must be made and results reported for all samples. If the on-column concentration of any target compound in any sample exceeds the initial calibration range, a new aliquot of that sample must be diluted and purged. Guidance for performing dilutions and exceptions to this requirement are given in Sections 10.2.9.2 through 10.2.9.8.

NOTE 1: If the laboratory has evidence or highly suspects, because of sample color or other physical property, that a sample may contain high concentrations of either target or non-target



compounds, then SMO shall be contacted immediately. SMO will seek regional recommendations for diluted analysis.

NOTE 2: Secondary ion quantitation is only allowed when there are sample interferences with the primary quantitation ion, not when saturation occurs. If secondary ion quantitation is used, calculate a Relative Response Factor (RRF) using the area response (EICP) from the most intense secondary ion which is free of sample interferences, and document the reasons in the SDG Narrative.

- 10.2.9.2 Use the results of the original analysis to determine the approximate dilution factor required to get the largest analyte peak within the initial calibration range.
- 10.2.9.3 The dilution factor chosen should keep the concentration of the volatile target compounds that required dilution in the upper half of the initial calibration range.
- 10.2.9.4 All dilutions must be made just prior to GC/MS analysis of the sample. Until the diluted sample is in a gas-tight syringe, all steps in the dilution procedure must be performed without delay.
- 10.2.9.5 Samples may be diluted in a volumetric flask or in a 25 mL "Luerlock" syringe.
- 10.2.9.6 To dilute the sample in a volumetric flask, use the following procedure:
  - 10.2.9.6.1 Select the volumetric flask that will allow for necessary dilution (25 mL to 100 mL).
  - 10.2.9.6.2 Calculate the approximate volume of reagent water which will be added to the volumetric flask selected and add slightly less than this quantity of reagent water to the flask.
  - 10.2.9.6.3 Inject the proper sample aliquot from a syringe into the volumetric flask. Only aliquots of 1 mL increments are permitted. Dilute the aliquot to the mark with reagent water. Cap the flask and invert it three times.
  - 10.2.9.6.4 Fill a 25 mL syringe with the diluted sample and analyze according to Section 10.2.
- 10.2.9.7 To dilute the sample in a 25 mL syringe, use the following procedure:
  - 10.2.9.7.1 Calculate the volume of the reagent water necessary for the dilution. The final volume of the diluted sample should be 25 mL.
  - 10.2.9.7.2 Close the syringe valve, remove the plunger from the syringe barrel, and pour reagent water into the syringe barrel to just short of overflowing.

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- 10.2.9.7.3        Replace the syringe plunger and compress the water.
- 10.2.9.7.4        Invert the syringe, open the syringe valve, and vent any residual air. Adjust the water volume to the desired amount.
- 10.2.9.7.5        Adjust the plunger to the 25 mL mark to accommodate the sample aliquot. Inject the proper aliquot of sample from another syringe through the valve bore of the 25 mL syringe. Close the valve and invert three times. Analyze according to Section 10.2.
- 10.2.9.8        For total xylenes where three isomers are quantified as two peaks, the calibration of each peak should be considered separately, e.g., a diluted analysis is not required for total xylenes unless the concentration of the peak representing the single isomer exceeds 25 micrograms per liter ( $\mu\text{g/L}$ ) on-column, or the peak representing the two co-eluting isomers exceeds 50  $\mu\text{g/L}$  on-column.

## 11.0 DATA ANALYSIS AND CALCULATIONS

### 11.1 Qualitative Identification of Target Compounds

- 11.1.1 The compounds listed in the Target Compound List (TCL), Exhibit C (Volatiles), shall be identified by an analyst competent in the interpretation of mass spectra by comparison of the sample mass spectrum to the mass spectrum of a standard of the suspected compound. Two criteria must be satisfied to verify the identifications:
- Elution of the sample component at the same Gas Chromatograph (GC) Relative Retention Time (RRT) as the standard component; and
  - Correspondence of the sample component and calibration standard component mass spectra.
- 11.1.2 For establishing correspondence of the GC RRT, the sample component RRT must be within  $\pm 0.06$  RRT units of the RRT of the standard component. For reference, the standard must be run in the same 12-hour time period as the sample. If samples are analyzed during the 12-hour time period as the initial calibration, use the RRT values from the 5 micrograms per liter ( $\mu\text{g/L}$ ) standard. If co-elution of interfering compounds prohibits accurate assignment of the sample component RRT from the total ion chromatogram, then the RRT should be assigned using the Extracted Ion Current Profile (EICP) for ions unique to the component of interest.
- 11.1.3 For comparison of standard and sample component mass spectra, mass spectra obtained on the Contractor's GC/MS are required. Once obtained, these standard spectra may be used for identification purposes, only if the Contractor's GC/MS meets the daily instrument performance requirements for 4-Bromofluorobenzene (BFB). These standard spectra may be obtained from the standard analysis that was also used to obtain the RRTs.
- 11.1.4 The guidelines for qualitative verification by comparison of mass spectra are as follows:
- 11.1.4.1 All ions present in the standard mass spectra at a relative intensity greater than 10 percent (most abundant ion in the spectrum equals 100 percent) must be present in the sample spectrum.
- 11.1.4.2 The relative intensities of ions specified in Section 11.1.4.1 must agree within  $\pm 20$  percent between the standard and sample spectra. (Example: For an ion with an abundance of 50 percent in the standard spectra, the corresponding sample abundance must be between 30 and 70 percent.)
- 11.1.4.3 Ions greater than 10 percent in the sample spectrum but not present in the standard spectrum must be considered and accounted for by the analyst making the comparison. The verification process should favor false positives. All compounds meeting the identification criteria must be reported with their spectra. For

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all compounds below the Contract Required Quantitation Limit (CRQL), report the actual value followed by a "J" (e.g., "0.3J").

- 11.1.4.4 If a compound cannot be verified by all of the spectral identification criteria listed in Section 11.1.4, but in the technical judgment of the mass spectral interpretation specialist, the identification is correct, then the Contractor shall report that identification and proceed with quantitation.

11.2 Qualitative Identification of Non-Target Compounds

- 11.2.1 A library search shall be executed for non-target sample components for the purpose of tentative identification. The NIST/EPA/NIH (May 1992 release or later) and/or Wiley (1991 release or later) or equivalent mass spectral library, shall be used as the reference library.

- 11.2.2 Up to 30 organic compounds of greatest apparent concentration not listed in Exhibit C for the volatile or semivolatile organic fraction, excluding the Deuterated Monitoring Compounds (DMCs) and internal standard compounds, shall be tentatively identified via a forward search of the NIST/EPA/NIH (May 1992 release or later) and/or Wiley (1991 release or later), or equivalent mass spectral library. The following are not to be reported:

- Compounds with a response of less than 10 percent of the internal standard (as determined by inspection of the peak areas or heights);
- Compounds which elute earlier than 30 seconds before the first purgeable compound listed in Exhibit C (Volatiles) or three minutes after the last purgeable compound listed in Exhibit C (Volatiles) are not required to be searched in this fashion;
- Carbon dioxide; and
- Semivolatile TCL compounds listed in Exhibit C.

Only after visual comparison of sample spectra with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification.

NOTE: Computer-generated library search routines must not use normalizations which would misrepresent the library or unknown spectra when compared to each other.

- 11.2.3 Up to 20 peaks of greatest apparent concentration (as determined by inspection of peak areas or heights) that are suspected to be straight-chain, branched, or cyclic alkanes, alone or part of an alkane series, shall be library searched. Documentation for the tentative identification must be supplied. Alkanes are not counted as part of the 30 organic compounds described in Section 11.2.2.

- 11.2.4 Guidelines for making tentative identification:
- 11.2.4.1 All major ions present in the reference mass spectrum at a relative intensity greater than 10 percent (most abundant ion in the spectrum equals 100 percent) must be present in the sample spectrum.
  - 11.2.4.2 The relative intensities of the major ions specified in Section 11.2.4.1 must agree within  $\pm 20$  percent between the reference and sample spectra. (Example: For an ion with an abundance of 50 percent in the reference spectrum, the corresponding sample ion abundance must be between 30 and 70 percent.)
  - 11.2.4.3 Molecular ions present in the reference spectrum should be present in the sample spectrum.
  - 11.2.4.4 Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.
  - 11.2.4.5 Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting compounds. Data system library reduction programs can sometimes create these discrepancies.
  - 11.2.4.6 Non-target compounds receiving a library search match of 85 percent or higher should be considered a "probable match". The compound should be reported unless the mass spectral interpretation specialist feels there is just evidence not to report the compound as identified by the library search program. The lab should include in the Sample Delivery Group (SDG) Narrative the justification for not reporting a compound as listed by the search program.
  - 11.2.4.7 If the library search produces more than one compound at or above 85 percent, report the compound with the highest percent match (report first compound if percent match is the same for two or more compounds), unless the mass spectral interpretation specialist feels that the highest match compound should not be reported, or another compound with a lower match should be reported. The lab should include in the SDG Narrative the justification for not reporting the compound with the highest spectral match.
  - 11.2.4.8 If the library search produces a series of obvious isomer compounds with library search matches greater than 85 percent (e.g., tetramethyl naphthalenes), the compound with the highest library search percent match should be reported (or first compound if library search matches are the same). A note should be placed in the SDG Narrative indicating the exact isomer configuration, as reported, may not be accurate.
  - 11.2.4.9 If the library search produces no matches at or above 85 percent and in the technical judgement of the mass spectral interpretation

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specialist, no valid tentative identification can be made, the compound should be reported as unknown. The mass spectral specialist should give additional classification of the unknown compound, if possible (e.g., unknown aromatic, unknown hydrocarbon, unknown acid type, unknown chlorinated compound). If probable molecular weights can be distinguished, include them.

- 11.2.4.10 Straight-chain, branched, or cyclic alkanes are not to be reported as tentatively identified compounds on Form I LCV-TIC. When the above alkanes are tentatively identified, the concentration(s) are to be estimated as described in Section 11.3.2 and reported in the SDG Narrative as alkanes, by class (i.e., straight-chain, branched, or cyclic, as a series, as applicable).

11.3 Calculations

11.3.1 Target Compounds

- 11.3.1.1 Target compounds identified shall be quantified by the internal standard method using Equation 6. The internal standard used shall be that which is assigned in Table D-3. The Relative Response Factor (RRF) from the continuing calibration standard is used to calculate the concentration in the sample. When a target compound concentration is below its CRQL but the spectra meets the identification criteria, report the concentration with a "J". For example, if the CRQL is 0.50 µg/L and a concentration of 0.30 µg/L is calculated, report as "0.30 J". Report ALL sample concentration data as UNCORRECTED for blanks.

EQ. 6

$$\text{Concentration in } \mu\text{g/L} = \frac{(A_x) (I_s) (Df)}{(A_{is}) (RRF) (V_o)}$$

Where:

- $A_x$  = Area of the characteristic ion (EICP) for the compound to be measured. The primary quantitation ions for the target compounds, internal standards, and the DMCs are listed in Table D-4.
- $A_{is}$  = Area of the characteristic ion (EICP) for the internal standard. The target compounds are listed with their associated internal standards in Table D-3.
- $I_s$  = Amount of internal standard added in nanograms (ng).
- RRF = The relative response factor from the continuing calibration standard.
- $V_o$  = Total volume of water purged, in milliliters (mL).

Df = Dilution factor. The dilution factor for analysis of water samples for volatiles by this method is defined as the ratio of the number of milliliters (mL) of water purged (i.e.,  $V_0$  above) to the number of mL of the original water sample used for purging. For example, if 5.0 mL of sample is diluted to 25.0 mL with reagent water and purged,  $Df = 25.0 \text{ mL} / 5 \text{ mL} = 5.0$ . If no dilution is performed,  $Df = 1.0$ .

- 11.3.1.2 Xylenes (o-, m-, and p- isomers) are to be reported as xylenes (total). Because o- and p-xylene isomers coelute on capillary columns, special attention must be given to the quantitation of the xylenes. The RRF determined in Section 9.4.4.1, is based on the peak that represents the single isomer on the GC column (o-xylene on capillary columns). In quantitating sample concentrations, use the areas on both peaks and the RRF. The areas of the two peaks may be summed and the concentration determined, or the concentration represented by each of the two peaks may be determined separately and then summed.
- 11.3.1.3 The stereoisomers, trans-1,2-dichloroethene, and cis-1,2-dichloroethene, are to be reported separately.
- 11.3.1.4 The requirements listed in Sections 11.3.1.5 and 11.3.1.6 apply to all standards, samples, and blanks.
- 11.3.1.5 It is expected that situations will arise where the automated quantitation procedures in the GC/MS software provide inappropriate quantitation. This normally occurs when there is compound co-elution, baseline noise, or matrix interferences. In these circumstances the Contractor must perform a manual quantitation. Manual quantitations are performed by integrating the area of the quantitation ion of the compound. This integration shall only include the area attributable to the specific TCL, deuterated monitoring, or internal standard compound. The area integrated shall not include baseline background noise. The area integrated shall not extend past the point where the sides of the peak intersect with the baseline noise. Manual integration is not to be used solely to meet QC criteria, nor is it to be used as a substitute for corrective action on the chromatographic system. Any instances of manual integration must be documented in the SDG Narrative.
- 11.3.1.6 In all instances where the data system report has been edited, or where manual integration or quantitation has been performed, the GC/MS operator must identify such edits or manual procedures by initialing and dating the changes made to the report, and shall include the integration scan range. In addition, a hardcopy printout of the EICP of the quantitation ion displaying the manual integration shall be included in the raw data. This applies to all compounds listed in Exhibit C (Volatiles), internal standard, and DMCs.

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11.3.2 Non-Target Compounds

11.3.2.1 An estimated concentration for non-target compounds tentatively identified shall be determined by the internal standard method. For quantitation, the nearest internal standard free of interferences shall be used.

11.3.2.2 Equation 6 is also used for calculating non-target compound concentrations. Total area counts (or peak heights) from the total Reconstructed Ion Chromatograms (RICs) are to be used for both the non-target compound to be measured ( $A_x$ ) and the internal standard ( $A_{is}$ ). A RRF of 1.0 is to be assumed. The value from this quantitation shall be qualified by a "J" (estimate due to lack of a compound-specific relative response factor), and "N" (presumptive evidence of presence), indicating the qualitative and quantitative uncertainties associated with this non-target compound. An estimated concentration must be calculated for all tentatively identified compounds as well as those identified as unknowns.

11.3.3 CRQL Calculation

Calculate the adjusted CRQL for volatiles by using Equation 7.

EQ. 7

$$\frac{\text{Adjusted CRQL}}{\text{Contract CRQL}} = \frac{V_o}{V_c} * Df$$

Where:

Contract CRQL = Exact CRQL values in Exhibit C of the SOW.

$V_o$  = Total volume of water purged in milliliters.  
NOTE: Must not exceed the contract sample volume.

$V_c$  = Contract sample volume in milliliters (25 mL).

$Df$  = Same as EQ. 6.

NOTE: If the adjusted CRQL is less than the CRQL listed in Exhibit C (Volatiles), report the CRQL listed in Exhibit C (Volatiles).

11.3.4 Deuterated Monitoring Compound Recoveries

11.3.4.1 Calculate the concentration of each DMC using the same equation as used for target compounds (Equation 6).

11.3.4.2 Calculate the recovery of each DMC in all samples and blanks using Equation 8. Report the recoveries on appropriate forms.



EQ. 8

$$\text{Percent Recovery} = \frac{Q_d}{Q_a} \times 100$$

Where:

$Q_d$  = Concentration or amount determined by analysis.

$Q_a$  = Concentration or amount added to sample/blank.

#### 11.3.5 Internal Standard Responses and Retention Times

Internal standard responses and retention times in all samples and blanks must be evaluated during or immediately after data acquisition. Compare the sample/blank internal standard responses and retention times to the continuing calibration internal standard responses and retention times. For samples and blanks analyzed during the same 12-hour time period as the initial calibration standards, compare the internal standard responses and retention times against the 5 µg/L calibration standard. The EICP of the internal standards must be monitored and evaluated for each sample and blank.

#### 11.4 Technical Acceptance Criteria for Sample Analysis

- 11.4.1 The sample must be analyzed on a GC/MS system meeting the BFB, initial calibration, continuing calibration, and blank technical acceptance criteria.
- 11.4.2 The sample and any required dilution must be analyzed within the contract holding time.
- 11.4.3 The sample must have an associated method blank meeting the blank technical acceptance criteria.
- 11.4.4 The percent recovery of each of the DMCs in the sample must be within the acceptance windows in Table D-5. Up to three DMCs per sample may fail to meet the recovery limits listed in Table D-5.
- 11.4.5 The EICP area for each of the internal standards in the sample must be within the inclusive range of ±40.0 percent of its response in the most recent continuing calibration standard analysis.
- 11.4.6 The retention time shift for each of the internal standards in the sample must be within ±0.33 minutes (20.0 seconds) of its retention time in the most recent continuing calibration standard analysis.
- 11.4.7 The RRT of each of the DMCs in the sample must be within ±0.06 RRT units of its relative retention time in the most recent continuing calibration standard analysis.

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- 11.4.8 Excluding those ions in the solvent front, no ion may saturate the detector. No target compound concentration may exceed the upper limit of the initial calibration range unless a more dilute aliquot of the sample is also analyzed according to the procedures in Section 10.2.9.
- 11.4.9 The Contractor must demonstrate that there is no carryover from a contaminated sample before data from subsequent analyses may be submitted. After a sample that contains a target compound at a level exceeding the initial calibration range, or a non-target compound at a concentration greater than 100 µg/L, or saturated ions from a compound (excluding the compound peaks in the solvent front), the Contractor must either:
- 11.4.9.1 Analyze an instrument blank immediately after the contaminated sample. If an autosampler is used, an instrument blank must also be analyzed using the same purge inlet that was used for the contaminated sample. The instrument blanks must meet the technical acceptance criteria for blank analysis (Section 12.1.5);  
or
- 11.4.9.2 Monitor the analyzed sample immediately after the contaminated sample for all the compounds that were in the contaminated sample and that exceeded the limits above. The maximum carryover criteria are as follows: the sample must not contain a concentration above the CRQL for the target compounds, or above 2 µg/L for the non-target compounds that exceeded the limits in the contaminated sample. If an autosampler is used, the next sample analyzed using the same purge inlet that was used for the contaminated sample must also meet the maximum carryover criteria.
- 11.5 Corrective Action for Sample Analysis
- 11.5.1 Sample technical acceptance criteria must be met before data are reported. Samples contaminated from laboratory sources or any samples not meeting the sample technical acceptance criteria will require re-analysis at no additional cost to USEPA.
- 11.5.2 Corrective actions for failure to meet instrument performance checks, initial calibration, continuing calibration, and method blanks must be completed before the analysis of samples.
- 11.5.3 If the technical acceptance criteria for any of the internal standards and DMCs are not met, check calculations, internal standard and DMC spiking solutions, and instrument performance. It may be necessary to bake-out the system to remove the water from the purge and trap transfer lines, to recalibrate the instrument, or take other corrective action procedures to meet the technical acceptance criteria.
- 11.5.4 Sample reruns performed as a result of suspected matrix interference beyond the scope of the method will be evaluated on a case-by-case basis for payment purposes by the USEPA Contract Laboratory Program Project Officer (CLP PO). Send a copy of the SDG Narrative

(including your contract number), a description of the situation, and the requested action to the CLP PO.

- 11.5.5 If the contractor needs to analyze more than one (1) sample dilution other than the original analysis to have all the target compounds within the initial calibration range, contact Sample Management Office (SMO). SMO will contact the Region for instruction.
- 11.5.6 All samples to be reported to USEPA must meet the maximum carryover criteria in Section 11.4.9. If any sample fails to meet these criteria, each subsequent analysis must be checked for cross contamination. The analytical system is considered contaminated until a sample has been analyzed that meets the maximum carryover criteria or an instrument blank has been analyzed that meets the technical acceptance criteria for blanks.

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Quality Control

12.0 QUALITY CONTROL (QC)

12.1 Blank Analyses

12.1.1 Summary of Blank Analyses

There are three different types of blanks required by this method.

12.1.1.1 Method Blank - 25 milliliters (mL) of reagent water spiked with 10.0 microliters (µL) internal standard solution and 10.0 µL Deuterated Monitoring Compound (DMC) solution, and carried through the entire analytical procedure. The purpose of the method blank is to determine the levels of contamination associated with processing and analysis of samples.

12.1.1.2 Storage Blank - Upon receipt of the first samples in a Sample Delivery Group (SDG), two 40 mL screw cap VOA vials with a PTFE-faced silicone septum are filled with reagent water (80 mL total). The vials are stored with the samples in the SDG under the same conditions. A 25.0 mL aliquot of this reagent water is spiked with a 10.0 µL internal standard solution and 10.0 µL of DMC solution and analyzed after all samples in the SDG have been analyzed. The storage blank indicates whether contamination may have occurred during storage of samples.

12.1.1.3 Instrument Blank - 25 mL of reagent water spiked with 10.0 µL of internal standard solution and 10.0 µL of DMC solution and carried through the entire analytical procedure. Instrument blanks are analyzed after a sample/dilution which contains a target compound at a concentration greater than 25 micrograms per liter (µg/L) (ketones 125 µg/L), or a non-target compound at a concentration greater than 100 µg/L or saturated ions from a compound (excluding the compound peaks in the solvent front). The results from instrument blank analysis indicate whether there is contamination from a previous sample.

12.1.2 Frequency of Blank Analyses

12.1.2.1 The method blank must be analyzed at least once during every 12-hour time period on each Gas Chromatograph/Mass Spectrometer (GC/MS) system used for volatile analysis (see Section 9.2.2 for the definition of the 12-hour time period).

12.1.2.2 The method blank must be analyzed after the continuing calibration standard and before any samples or storage blanks are analyzed. The method blank must be analyzed after the initial calibration sequence if samples are analyzed before the 12-hour time period expires. A method blank must be analyzed in each 12-hour time period in which samples (including dilutions) and storage blanks from an SDG are analyzed.

12.1.2.3 A minimum of one storage blank must be analyzed per SDG, after all samples for the SDG have been analyzed, unless the SDG contains only ampulated Performance Evaluation (PE) samples. Analysis of a

storage blank is not required for SDGs that contain only ampulated PE samples.

- 12.1.2.4 The Contractor must demonstrate that there is no carryover from contaminated samples before data from subsequent analyses may be used. Samples may contain target compounds at levels exceeding the initial calibration range or non-target compounds at concentrations greater than 100 µg/L, or ions from a compound that saturate the detector (excluding the compound peaks in the solvent front). An instrument blank must be analyzed immediately after the contaminated sample (also in the same purge inlet if an autosampler is used), or a sample that meets the maximum carryover criteria in Section 11.4.9 must be analyzed. For these purposes, if the instrument blank meets the technical acceptance criteria for blank analysis or the sample meets the maximum carryover criteria, the system is considered to be uncontaminated. If the instrument blank or sample does not meet the criteria (i.e., contaminated), the system must be decontaminated. Until an instrument blank meets the blank technical acceptance criteria or a sample meets the maximum carryover criteria, any samples analyzed since the original contaminated sample will require re-analysis at no additional expense to USEPA.

NOTE: Only the instrument blank which demonstrates that there was no carryover from the previous sample or the instrument blank that demonstrates that the system is clean (Section 12.1.5.7) must be reported. Instrument blanks analyzed during the instrument decontamination process which exceed the requirements listed in Section 11.4.9 do not need to be reported.

12.1.3 Procedure for Blank Analyses

- 12.1.3.1 Spike 25 mL of reagent water with 10.0 µL of the internal standard solution (Section 7.2.3.3), and 10.0 µL of the DMC solution (Section 7.2.3.4).

- 12.1.3.2 Prepare and analyze the blanks as described in Section 10.2.

12.1.4 Calculations for Blank Analyses

Perform data analysis and calculations according to Section 11.

12.1.5 Technical Acceptance Criteria for Blank Analyses

- 12.1.5.1 All blanks must be analyzed on a GC/MS system meeting the 4-Bromo-fluorobenzene (BFB), initial calibration, and continuing calibration technical acceptance criteria, and at the frequency described in Section 12.1.2.
- 12.1.5.2 The storage blank must be analyzed on a GC/MS system that also meets the technical acceptance criteria for the method blank.
- 12.1.5.3 The percent recovery of each of the DMCs in the blank must be within the acceptance windows in Table D-5.

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- 12.1.5.4 The EICP area for each of the internal standards in the blank must be within the inclusive range of  $\pm 40.0$  percent of its response in the most recent continuing calibration standard analysis.
- 12.1.5.5 The retention time shift for each of the internal standards in the blank must be within  $\pm 0.33$  minutes (20.0 seconds) of its retention time in the most recent continuing calibration standard analysis.
- 12.1.5.6 The Relative Retention Time (RRT) of each of the DMCs in the blank must be within  $\pm 0.06$  RRT units of its relative retention time in the most recent continuing calibration standard analysis.
- 12.1.5.7 The concentration of each target compound found in the storage and method blanks must be less than its CRQL listed in Exhibit C (Volatiles), except for methylene chloride and cyclohexane which must be less than 10 times their respective CRQLs, and acetone and 2-butanone, which must be less than two times their respective CRQLs. The concentration of each target compound in the instrument blank must be less than its CRQL listed in Exhibit C (Volatiles). The concentration of non-target compounds in all blanks must be less than 2.0  $\mu\text{g/L}$ .
- 12.1.6 Corrective Action for Blank Analyses
- 12.1.6.1 It is the Contractor's responsibility to ensure that method interferences caused by contaminants in solvents, reagents, glassware, laboratory air, and other sample storage and processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms, be eliminated. If a Contractor's blanks exceed the criteria in Section 12.1.5.7, the Contractor must consider the analytical system to be out of control. The source of the contamination must be investigated and appropriate corrective measures MUST be taken and documented before further sample analysis proceeds.
- 12.1.6.2 Any method blank or instrument blank that fails to meet the technical acceptance criteria must be re-analyzed at no additional cost to USEPA. Further, all samples processed within the 12-hour time period with a method blank or instrument blank that does not meet the blank technical acceptance criteria will require re-analysis at no additional cost to USEPA.
- 12.1.6.3 If the storage blank does not meet the technical acceptance criteria for blank analyses in Sections 12.1.5.1 to 12.1.5.6, correct system problems and re-analyze the storage blank. If the storage blank does not meet the criteria in Section 12.1.5.7, re-analyze the blank to determine whether the contamination occurred during storage or during analyses. If upon re-analysis, the storage blank meets the criteria in Section 12.1.5.7, the problem occurred during the analysis and the re-analyzed storage blank results must be reported. If upon re-analysis the storage blank did not meet the criteria in Section 12.1.5.7, the problem occurred during storage. The laboratory manager or his/her designee must address the problem in the SDG Narrative and discuss the corrective actions implemented to prevent future occurrences.

NOTE: A copy of the storage blank data must be retained by the Contractor and be made available for inspection during on-site laboratory evaluations.

12.2 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

12.2.1 Summary of MS/MSD

In order to evaluate the effects of the sample matrix on the method used for volatile analysis, USEPA has prescribed a mixture of volatile target compounds to be spiked into two aliquots of a sample, and analyzed in accordance with the appropriate method, upon request.

12.2.2 Frequency of MS/MSD

- 12.2.2.1 A MS/MSD shall only be analyzed if requested by the Region (through the Sample Management Office (SMO)) or specified on the Traffic Report (TR). If requested, a matrix spike and a matrix spike duplicate must be performed for each group of 20 field samples in an SDG, or each SDG, whichever is most frequent.
- 12.2.2.2 As part of USEPA's Quality Assurance (QA)/Quality Control (QC) program, water rinsate samples and/or field/trip blanks (field QC) may be delivered to a laboratory for analysis. The Contractor shall not perform MS/MSD analysis on any of the field QC samples.
- 12.2.2.3 If the USEPA Region requesting MS/MSD designates a sample to be used as an MS/MSD, then that sample must be used. If there is insufficient sample, less than the required amount, remaining to perform an MS/MSD, then the Contractor shall choose another sample to perform an MS/MSD analysis. At the time the selection is made, the Contractor shall notify the Region (through SMO) that insufficient sample was received and identify the USEPA sample selected for the MS/MSD analysis. The rationale for the choice of a sample other than the one designated by the Region shall be documented in the SDG Narrative.
- 12.2.2.4 If there is insufficient sample remaining in any of the samples in an SDG to perform an MS/MSD, then the Contractor shall immediately contact SMO to inform them of the problem. SMO will contact the Region for instructions. The Region will either approve that no MS/MSD is required, or require that a reduced sample aliquot be used for the MS/MSD analysis. SMO will notify the Contractor of the resolution. The Contractor shall document the decision in the SDG Narrative.
- 12.2.2.5 If it appears that the Region has requested MS/MSD analysis at a greater frequency than specified in Section 12.2.2.1, the Contractor shall contact SMO. SMO will contact the Region to determine which samples should have an MS/MSD performed on them. SMO will notify the Contractor of the Region's decision. The Contractor shall document the decision in the SDG Narrative. If this procedure is not followed, the Contractor will not be paid for MS/MSD analysis performed at a greater frequency than required by the contract.

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- 12.2.2.6 When a Contractor receives **only** Performance Evaluation (PE) sample(s), no MS/MSD shall be performed within that SDG.
- 12.2.2.7 When a Contractor receives a PE sample as part of a larger SDG, a sample other than the PE sample must be chosen for the requested MS/MSD analysis when the Region did not designate samples to be used for this purpose.
- 12.2.3 Procedure for Preparing MS/MSD
- 12.2.3.1 To prepare MS/MSD samples, add 10 µL of the matrix spike solution (Section 7.2.3.5) to each of the 25 mL aliquots of the sample chosen for spiking. Process samples according to Section 10.2. Disregarding any dilutions, this is equivalent to a concentration of 5 µg/L of each matrix spike compound.
- 12.2.3.2 MS/MSD samples must be analyzed at the same concentration as the most concentrated aliquot for which the original sample results will be reported. Sample dilutions must be performed in accordance with Section 10.2.9. Do **not** further dilute MS/MSD samples to get **either** spiked **or** non-spiked analytes within calibration range.
- 12.2.4 Calculations for MS/MSD
- 12.2.4.1 Calculate the concentrations of the matrix spike compounds using the same equations as used for target compounds (Equation 6). Calculate the recovery of each matrix spike compound as follows:

EQ. 9

$$\text{Matrix Spike Recovery} = \frac{\text{SSR} - \text{SR}}{\text{SA}} \times 100$$

Where:

SSR = Spiked sample result.

SR = Sample result.

SA = Spike added.

- 12.2.4.2 Calculate the Relative Percent Difference (RPD) of the recoveries of each compound in the MS/MSD as follows:

EQ. 10

$$\text{RPD} = \frac{|\text{MSR} - \text{MSDR}|}{\frac{1}{2}(\text{MSR} + \text{MSDR})} \times 100$$



Where:

MSR = Matrix spike recovery.

MSDR = Matrix spike duplicate recovery.

#### 12.2.5 Technical Acceptance Criteria for MS/MSD

- 12.2.5.1 If requested, all MS/MSD must be prepared and analyzed at the frequency described in Section 12.2.2. All MS/MSDs must be analyzed on a GC/MS system meeting the BFB, initial and continuing calibration technical acceptance criteria, and the blank technical acceptance criteria.
- 12.2.5.2 The MS/MSD must be analyzed within the contract holding time.
- 12.2.5.3 The retention time shift for each of the internal standards in the MS/MSD must be within  $\pm 0.33$  minutes (20 seconds) of its retention time in the most recent continuing calibration standard analysis.
- 12.2.5.4 The limits for matrix spike compound recovery and RPD are given in Table D-6. As these limits are only advisory, no further action by the laboratory is required. However, frequent failures to meet the limits for recovery or RPD warrant investigation by the laboratory, and may result in questions from USEPA.
- 12.2.5.5 The relative retention time for the DMCs must be within  $\pm 0.06$  RRT units of its standard retention time in the Continuing Calibration Standard.

#### 12.2.6 Corrective Action for MS/MSD

Any MS/MSD that does not meet the technical acceptance criteria in Sections 12.2.5.1 through 12.2.5.3 must be re-analyzed at no additional cost to USEPA.

#### 12.3 Method Detection Limit (MDL) Determination

- 12.3.1 Before any field samples are analyzed under this contract, the MDL for each volatile target compound shall be determined on each instrument used for analysis. The MDLs must be verified annually thereafter (see Section 12.3.2 for MDL verification procedures), until the contract expires or is terminated, or after major instrument maintenance. Major instrument maintenance includes, but is not limited to cleaning or replacement of the mass spectrometer source, mass filters (e.g., quadrupole, ion trap, etc.), or electron multiplier (or similar device), replacement of gas chromatographic column, and replacement or overhaul of the purge and trap device.
- 12.3.2 To determine the MDLs, the Contractor shall run an MDL study following the procedures specified in 40 CFR Part 136. The Contractor shall analyze the MDL samples on each instrument used for field sample analyses. MDL verification is achieved by analyzing a single reagent water blank spiked with each volatile target compound

Exhibit D Volatiles -- Section 12  
Quality Control (Con't)

- at a concentration equal to two times the analytical determined MDL.  
The resulting mass spectra of each target compound must meet the  
qualitative identification criteria outlined in Sections 11.1.1  
through 11.1.4.3
- 12.3.3 The determined concentration of the MDL must be less than the CRQL.
- 12.3.4 All documentation for the MDL studies shall be maintained at the  
laboratory and provided to USEPA upon written request.

13.0 METHOD PERFORMANCE

Not applicable.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. USEPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibility reduced at the source, USEPA recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions, consult *Less is Better: Laboratory Chemical Management for Waste Reduction*, available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street, N.W., Washington D.C., 20036, (202) 872-4477.

15.0 WASTE MANAGEMENT

15.1 USEPA requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. USEPA urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel*, available from the American Chemical Society at the address listed in Section 14.2.

16.0 REFERENCES

Not applicable.

17.0 TABLES/DIAGRAMS/FLOWCHARTS

TABLE D-1 BFB KEY IONS AND ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
50	8.0 - 40.0 percent of mass 95
75	30.0 - 66.0 percent of mass 95
95	base peak, 100 percent relative abundance
96	5.0 - 9.0 percent of mass 95 (see note)
173	less than 2.0 percent of mass 174
174	50.0 - 120.0 percent of mass 95
175	4.0 - 9.0 percent of mass 174
176	93.0 - 101.0 percent of mass 174
177	5.0 - 9.0 percent of mass 176

NOTE: All ion abundances must be normalized to m/z 95, the nominal base peak, even though the ion abundance of m/z 174 may be up to 120 percent that of m/z 95.

TABLE D-2  
TECHNICAL ACCEPTANCE CRITERIA FOR INITIAL AND CONTINUING  
CALIBRATION FOR VOLATILE ORGANIC COMPOUNDS

Volatile Compound	Minimum RRF	Maximum %RSD	Maximum %Diff
Dichlorodifluoromethane	0.010	none	none
Chloromethane	0.010	none	none
Vinyl chloride	0.100	30.0	±30.0
Bromomethane	0.100	30.0	±30.0
Chloroethane	0.010	none	none
Trichlorofluoromethane	0.010	none	none
1,1-Dichloroethene	0.100	30.0	±30.0
1,1,2-Trichloro-1,2,2-trifluoroethane	0.010	none	none
Acetone	0.010	none	none
Carbon disulfide	0.010	none	none
Methyl Acetate	0.010	none	none
Methylene chloride	0.010	none	none
trans-1,2-Dichloroethene	0.010	none	none
Methyl tert-Butyl Ether	0.010	none	none
1,1-Dichloroethane	0.200	30.0	±30.0
cis-1,2-Dichloroethene	0.010	none	none
2-Butanone	0.010	none	none
Bromochloromethane	0.050	30.0	±30.0
Chloroform	0.200	30.0	±30.0
1,1,1-Trichloroethane	0.100	30.0	±30.0
Cyclohexane	0.010	none	none
Carbon tetrachloride	0.100	30.0	±30.0
Benzene	0.400	30.0	±30.0
1,2-Dichloroethane	0.100	30.0	±30.0
Trichloroethene	0.300	30.0	±30.0
Methylcyclohexane	0.010	none	none
1,2-Dichloropropane	0.010	none	none
Bromodichloromethane	0.200	30.0	±30.0
cis-1,3-Dichloropropene	0.200	30.0	±30.0
4-Methyl-2-pentanone	0.010	none	none
Toluene	0.400	30.0	±30.0
trans-1,3-Dichloropropene	0.100	30.0	±30.0
1,1,2-Trichloroethane	0.100	30.0	±30.0
Tetrachloroethene	0.100	30.0	±30.0
2-Hexanone	0.010	none	none
Dibromochloromethane	0.100	30.0	±30.0
1,2-Dibromoethane	0.100	30.0	±30.0
Chlorobenzene	0.500	30.0	±30.0
Ethylbenzene	0.100	30.0	±30.0
Xylene (total)	0.300	30.0	±30.0
Styrene	0.300	30.0	±30.0
Bromoform	0.050	30.0	±30.0
Isopropylbenzene	0.010	none	none

TABLE D-2  
TECHNICAL ACCEPTANCE CRITERIA FOR INITIAL AND CONTINUING  
CALIBRATION FOR VOLATILE ORGANIC COMPOUNDS (Con't)

Volatile Compound	Minimum RRF	Maximum %RSD	Maximum %Diff
1,1,2,2-Tetrachloroethane	0.100	30.0	±30.0
1,3-Dichlorobenzene	0.400	30.0	±30.0
1,4-Dichlorobenzene	0.400	30.0	±30.0
1,2-Dichlorobenzene	0.400	30.0	±30.0
1,2-Dibromo-3-chloropropane	0.010	none	none
1,2,4-Trichlorobenzene	0.200	30.0	±30.0
1,2,3-Trichlorobenzene	0.200	30.0	±30.0
DEUTERATED MONITORING COMPOUNDS			
Vinyl Chloride-d3	0.010	none	none
Chloroethane-d5	0.010	none	none
1,1-Dichloroethene-d2	0.010	none	none
2-Butanone-d5	0.010	none	none
Chloroform-d	0.010	none	none
1,2-Dichloroethane-d4	0.010	none	none
Benzene-d6	0.010	none	none
1,2-Dichloropropane-d6	0.010	none	none
Toluene-d8	0.010	none	none
trans-1,3-Dichloropropene-d4	0.010	none	none
2-Hexanone-d5	0.010	none	none
Bromoform-d	0.010	none	none
1,1,2,2-Tetrachloroethane-d2	0.010	none	none
1,2-Dichlorobenzene-d4	0.010	none	none

TABLE D-3  
VOLATILE TARGET COMPOUNDS AND DEUTERATED MONITORING COMPOUND (DMC)  
WITH CORRESPONDING INTERNAL STANDARDS FOR QUANTITATION

1,4-Difluorobenzene	Chlorobenzene-d5	1,4-Dichlorobenzene-d4
Dichlorodifluoromethane	1,1,1-Trichloroethane	Bromoform
Chloromethane	Cyclohexane	1,3-Dichlorobenzene
Vinyl Chloride	Carbon Tetrachloride	1,4-Dichlorobenzene
Bromomethane	Benzene	1,2-Dichlorobenzene
Chloroethane	Trichloroethene	1,2-Dibromo-3-chloropropane
Trichlorofluoromethane	Methylcyclohexane	1,2,4-Trichlorobenzene
1,1-Dichloroethene	1,2-Dichloropropane	1,2,3-Trichlorobenzene
1,1,2-Trichloro-1,2,2-trifluoroethane	Bromodichloromethane	1,2-Dichlorobenzene-d4 (DMC)
Acetone	cis-1,3-Dichloropropene	Bromoform-d (DMC)
Carbon Disulfide	4-Methyl-2-pentanone	
Methyl Acetate	Toluene	
Bromochloromethane	trans-1,3-Dichloropropene	
Methylene Chloride	1,1,2-Trichloroethane	
trans-1,2-Dichloroethene	Tetrachloroethene	
Methyl tert-Butyl Ether	2-Hexanone	
1,1-Dichloroethane	Dibromochloromethane	
cis-1,2-Dichloroethene	1,2-Dibromoethane	
2-Butanone	Chlorobenzene	
Chloroform	Ethylbenzene	
1,2-Dichloroethane	Xylenes (total)	
Vinyl Chloride-d3 (DMC)	Styrene	
Chloroethane-d5 (DMC)	Isopropylbenzene	
1,1-Dichloroethene-d2 (DMC)	1,1,2,2-Tetrachloroethane	
2-Butanone-d5 (DMC)	Benzene-d6 (DMC)	
Chloroform-d (DMC)	1,2-Dichloropropane-d6 (DMC)	
1,2-Dichloroethane-d4 (DMC)	trans-1,3-Dichloropropene-d4 (DMC)	
	Toluene-d8 (DMC)	
	2-Hexanone-d5 (DMC)	
	1,1,2,2-Tetrachloroethane-d2 (DMC)	

TABLE D-4  
CHARACTERISTIC IONS FOR VOLATILE TARGET COMPOUNDS

Target Compound	Primary Quantitation Ion	Secondary Ion(s)
Dichlorodifluoromethane	85	87
Chloromethane	50	52
Vinyl chloride	62	64
Bromomethane	94	96
Chloroethane	64	66
Trichlorofluoromethane	101	103
1,1-Dichloroethene	96	61, 63
1,1,2-Trichloro-1,2,2-trifluoroethane	101	85, 151
Acetone	43	58
Carbon disulfide	76	78
Methyl Acetate	43	74
Methylene chloride	84	49, 86
trans-1,2-Dichloroethene	96	61, 98
Methyl tert-Butyl Ether	73	43, 57
1,1-Dichloroethane	63	65, 83
cis-1,2-Dichloroethene	96	61, 98
2-Butanone	43*	72
Chloroform	83	85
Bromochloromethane	128	49, 130, 51
1,1,1-Trichloroethane	97	99, 61
Cyclohexane	56	69, 84
Carbon Tetrachloride	117	119
Benzene	78	-
1,2-Dichloroethane	62	98
Trichloroethene	95	97, 132, 130
Methylcyclohexane	83	55, 98
1,2-Dichloropropane	63	112
Bromodichloromethane	83	85, 127
cis-1,3-Dichloropropene	75	77
4-Methyl-2-pentanone	43	58, 100
Toluene	91	92
trans-1,3-Dichloropropene	75	77
1,1,2-Trichloroethane	97	83, 85, 99, 132, 134
Tetrachloroethene	164	129, 131, 166
2-Hexanone	43	58, 57, 100
Dibromochloromethane	129	127
1,2-Dibromoethane	107	109, 188
Chlorobenzene	112	77, 114
Ethylbenzene	91	106
Xylene (total)	106	91
Styrene	104	78
Bromoform	173	175, 254

\*m/z 43 is used for quantitation of 2-Butanone, but m/z 72 must be present for positive identification.



TABLE D-4  
CHARACTERISTIC IONS FOR VOLATILE TARGET COMPOUNDS (Con't)

Analyte	Primary Quantitation Ion	Secondary Ion(s)
Isopropylbenzene	105	120, 77
1,1,2,2-Tetrachloroethane	83	85, 131
1,3-Dichlorobenzene	146	111, 148
1,4-Dichlorobenzene	146	111, 148
1,2-Dichlorobenzene	146	111, 148
1,2-Dibromo-3-Chloropropane	75	157, 155
1,2,4-Trichlorobenzene	180	182, 145
1,2,3-Trichlorobenzene	180	182, 145
Deuterated Monitoring Compounds		
Vinyl Chloride-d3	65	67
Chloroethane-d5	69	71, 51
1,1-Dichloroethene-d2	63	98, 65
2-Butanone-d5	46	77
Chloroform-d	84	86, 47, 49
1,2-Dichloroethane-d4	65	67, 51
Benzene-d6	84	82, 54, 52
1,2-Dichloropropane-d6	67	65, 46, 42
Toluene-d8	98	100, 42
trans-1,3-Dichloropropene-d4	79	81, 42
2-Hexanone-d5	63	46
Bromoform-d	174	172
1,1,2,2-Tetrachloroethane-d2	84	86
1,2-Dichlorobenzene-d4	152	150
Internal Standards		
1,4-Dichlorobenzene-d4	152	115, 150
1,4-Difluorobenzene	114	63, 88
Chlorobenzene-d5	117	82, 119

TABLE D-5  
DEUTERATED MONITORING COMPOUND RECOVERY LIMITS

Compound	Percent Recovery Limits
Vinyl Chloride-d3	49-138
Chloroethane-d5	60-126
1,1-Dichloroethene-d2	65-130
2-Butanone-d5	42-171
Chloroform-d	80-123
1,2-Dichloroethane-d4	78-129
Benzene-d6	78-121
1,2-Dichloropropane-d6	84-123
Toluene-d8	77-120
trans-1,3-Dichloropropene-d4	80-128
2-Hexanone-d5	37-169
Bromoform-d	76-135
1,1,2,2-Tetrachloroethane-d2	75-131
1,2-Dichlorobenzene-d4	50-150

NOTE: The recovery limits for any of the compounds listed above may be expanded at any time during the period of performance if USEPA determines that the limits are too restrictive.

TABLE D-6  
MATRIX SPIKE RECOVERY AND  
RELATIVE PERCENT DIFFERENCE LIMITS

Compound	% Recovery	RPD
1,1-Dichloroethene	61-145	14
Benzene	76-127	11
Trichloroethene	71-120	14
Toluene	76-125	13
Chlorobenzene	75-130	13

EXHIBIT D  
METHOD FOR THE ANALYSIS OF LOW CONCENTRATION WATER FOR  
SEMIVOLATILE ORGANIC COMPOUNDS

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# Exhibit D -- Analytical Methods for Semivolatiles

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1.0 SCOPE AND APPLICATION

1.1 The analytical method that follows is designed to analyze water samples containing low concentrations of the semivolatile compounds listed on the Target Compound List (TCL) in Exhibit C. The majority of the samples are expected to be from drinking water and well/ground water/aqueous type sources around Superfund sites. The method is based upon the semivolatile method contained in the Contract Laboratory Program (CLP) Statement of Work, "Organic Analysis, Multi-Media, Multi-Concentration Analyses". The analytical method includes the use of Deuterated Monitoring Compounds (DMC) for precision and accuracy assessment.

1.2 Benzaldehyde, Acetophenone, Caprolactam, 1,1'-Biphenyl, Atrazine, and 1,2,4,5-Tetrachlorobenzene have been added to the TCL.

1.3 Problems have been associated with the following compounds analyzed by this method:

- 3,3'-Dichlorobenzidine and 4-chloroaniline may be subject to oxidative losses during solvent concentration.
- Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the Gas Chromatograph (GC), chemical reactions in acetone solution, and photochemical decomposition.
- N-nitrosodiphenylamine decomposes in the gas chromatographic inlet forming diphenylamine and, consequently, may be detected as diphenylamine.
- Due to the lower quantitation limits required by this method, extra caution must be exercised when identifying compounds.

Exhibit D Semivolatiles -- Sections 2 & 3  
Summary of Method

2.0 SUMMARY OF METHOD

- 2.1 A one liter aliquot of sample is acidified to pH 2.0 and extracted with methylene chloride using a continuous liquid-liquid extractor. Separatory funnel extraction is not permitted. The methylene chloride extract is dried with sodium sulfate and concentrated to a volume of 1.0 milliliter (mL). The extract is injected onto a Gas Chromatograph (GC) capillary column. The GC is temperature programmed to separate the semivolatile compounds, which are then detected with a Mass Spectrometer (MS).
- 2.2 Deuterated Monitoring Compounds (DMCs) and internal standards are added to all samples, standards, requested Matrix Spike/Matrix Spike Duplicate(s) (MS/MSD) and blanks. The target compounds and DMCs are identified in the samples and blanks by analyzing standards that contain all target compounds, DMCs, and internal standards under the same conditions and comparing resultant mass spectra and GC retention times. A Relative Response Factor (RRF) is established for each target compound and DMC during the initial and continuing calibrations by comparing the mass spectra response from the Extracted Ion Current Profile (EICP) for the primary quantitation ion produced by that compound to the mass spectra response for the primary quantitation ion produced by the associated internal standard compound. Each identified target compound and DMC is quantitated by comparing the instrument response for the compound in the sample, standard, requested MS/MSD or blank with the instrument response of the associated internal standard, while taking into account the RRF from the most recent mid-point calibration, the sample volume, and any sample dilutions.
- 2.3 Non-target compounds are identified by comparing the resultant mass spectra from the non-target compounds to mass spectra contained in the NIST/EPA/NIH (May 1992 release or later) and/or Wiley (1991 release or later) or equivalent mass spectral library. Non-target compounds are quantitated by comparing the mass spectra response from the Reconstructed Ion Chromatogram (RIC) for the non-target compound peaks to the mass spectra response produced by the nearest internal standard. An RRF of 1 is assumed.

3.0 DEFINITIONS

See Exhibit G for a complete list of definitions.



#### 4.0 INTERFERENCES

Contaminants in solvents, reagents, glassware, and other sample processing hardware may cause method interferences such as discrete artifacts and/or elevated baselines in the Reconstructed Ion Chromatogram (RIC) profiles. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory method blanks. Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source.

#### 5.0 SAFETY

The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these reagents should be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets should be made available to all personnel involved in these analyses. Specifically, concentrated sulfuric acid presents some hazards and is moderately toxic and extremely irritating to skin and mucous membranes. Use these reagents in a fume hood whenever possible and if eye or skin contact occurs flush with large volumes of water. Always wear safety glasses or a shield for eye protection, protective clothing, and observe proper mixing when working with these reagents.

Exhibit D Semivolatiles -- Section 6  
Equipment and Supplies

6.0 EQUIPMENT AND SUPPLIES

Brand names, suppliers, catalog and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and supplies other than those specified here, but demonstration of equivalent performance meeting the requirements of this Statement of Work is the responsibility of the Contractor. The Contractor shall document any use of alternate equipment or supplies in the SDG Narrative.

6.1 Glassware

- 6.1.1 Continuous liquid-liquid extractors - Equipped with PTFE or glass connecting joints and stopcocks requiring no lubrication (Hershberg-Wolf Extractor-Ace Glass Company, Vineland, NJ, P/N 6841-10 or equivalent) or Hydrophobic Membrane-based Extractor (Accelerated One Step™ Extractor, Corning series 3195 or equivalent).
- 6.1.2 Drying column - 19 millimeter (mm) ID chromatographic column with coarse frit (substitution of a small pad of Pyrex pre-extracted glass wool for the frit will prevent cross contamination of sample extracts).
- 6.1.3 Kuderna-Danish Apparatus
  - 6.1.3.1 Concentrator tube - Kuderna-Danish, 10 milliliter (mL), graduated (Kontes, Vineland, NJ, K-570050-1025 or equivalent).
  - 6.1.3.2 Evaporation flask - Kuderna-Danish, 500 mL (Kontes K-570001 -0500 or equivalent). Attach to concentrator tube with springs.
  - 6.1.3.3 Snyder column - Kuderna-Danish, Three-ball macro (Kontes K-50300-0121 or equivalent).
  - 6.1.3.4 Snyder column - Kuderna-Danish, Two-ball micro (Kontes K-569001-0219 or equivalent).
- 6.1.4 Vials - Amber glass, 2 mL capacity with PTFE-lined screw-cap.
- 6.1.5 Syringes - 0.2 mL, 0.5 mL, 10 mL volumes with Luerlock.
- 6.1.6 Micro-syringes - 10 microliter (μL) and larger, 0.006 inch (0.15 mm) ID needle.
- 6.2 Gases - Helium, Nitrogen, ultra pure grade.
- 6.3 Gas-line Tubing - Stainless steel or copper tubing.
- 6.4 Silicon Carbide Boiling Chips - Approximately 10/40 mesh. Heat to 400°C for 30 minutes or Soxhlet extract with methylene chloride. PTFE boiling chips solvent rinsed prior to use are acceptable.
- 6.5 Water Bath - Heated, with concentric ring cover, capable of temperature control. To prevent the release of solvent fumes into the laboratory, the bath must be used in a hood.
- 6.6 Balance - Analytical, capable of accurately weighing ±0.0001 grams (g). The balances must be calibrated with class S weights or known reference weights once per each 12-hour workshift. The balances must be calibrated with class S weights at a minimum of once a month. The balances must also be annually checked by a certified technician.

- 6.7 Nitrogen Evaporation Device - Equipped with a water bath that can be maintained at 35°C to 40°C. To prevent the release of solvent fumes into the laboratory, the nitrogen evaporation device must be used in a hood. The N-Evap by Organomation Associates, Inc. South Berlin, MA (or equivalent) is suitable.
- 6.8 pH Meter - With a combination glass electrode, calibrated according to manufacturer's instructions. The pH meter shall be calibrated before each use.
- 6.9 pH Paper - Including narrow range capable of measuring a pH of 2.
- 6.10 Gas Chromatograph/Mass Spectrometer (GC/MS)
- 6.10.1 Gas Chromatograph - The gas chromatograph system must be capable of temperature programming and have a flow controller that maintains a constant column flow rate throughout the temperature program. The system must be suitable for splitless injection and have all required accessories including syringes, analytical columns, and gases. All GC carrier gas lines must be constructed from stainless steel or copper tubing. Non-polytetrafluoroethylene (PTFE) thread sealants, or flow controllers with rubber components are not to be used.
- 6.10.2 Gas Chromatography Column - Minimum length 30 meters (m) x 0.25 millimeter (mm) ID (or 0.32 mm) bonded-phase silicon coated fused silica capillary column DB-5 (J&W Scientific); RTx-5 (Restek); SPB-5 (Supelco); AT-5 (Alltech); HP-5 (Hewlett-Packard); CP-Sil 8CB (Chrompack); 007-2 (Quadrex); BP-5 (SGE); or equivalent. Note that this is a minimum requirement for column length. Longer columns may be used. Although a film thickness of 1.0 micron is recommended because of its larger capacity, a film thickness of 0.25 micron may be used. A description of the GC column used for analysis shall be provided in the SDG Narrative.
- 6.10.2.1 A capillary column is considered equivalent if:
- The column does not introduce contaminants which interfere with the identification and quantitation of the compounds listed in Exhibit C (Semivolatiles).
  - The analytical results generated using the column meet the initial and continuing calibration technical acceptance criteria listed in the SOW, and the Contract Required Quantitation Limits (CRQLs) listed in Exhibit C (Semivolatiles).
  - The column can accept up to 120 nanograms (ng) of each compound listed in Exhibit C (Semivolatiles) without becoming overloaded.
  - The column provides equal or better resolution of the compounds listed in Exhibit C (Semivolatiles) than the columns listed in Section 6.10.2.
- 6.10.2.2 As applicable, follow manufacturer's instructions for use of its product.
- 6.10.2.3 The Contractor must maintain documentation that the alternate column met the criteria in Section 6.10.2.1. The minimum documentation is as follows:

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- 6.10.2.3.1 Manufacturer provided information concerning the performance characteristics of the column.
- 6.10.2.3.2 Reconstructed Ion Chromatograms (RICs) and data system reports generated on the GC/MS used for CLP analyses:
- From blanks which demonstrate that there are no contaminants which interfere with the semivolatile analysis when using the alternate column;
  - For initial calibration standards analyzed using the alternate column;
  - For continuing calibration standards analyzed using the alternate column.
- 6.10.2.4 Based on the Contractor generated data described in Section 6.10.2.3.2, the Contractor must complete a written comparison and review signed by the Laboratory Manager certifying that:
- The column performance meets the technical acceptance criteria in Sections 9.3.5 and 9.4.5.
  - The low point initial calibration standard analysis has adequate sensitivity to meet the semivolatile CRQLs.
  - The high point initial calibration standard analysis was not overloaded.
  - The column does not introduce contaminants which interfere with the identification and/or quantitation of compounds listed in Exhibit C (Semivolatiles).
- 6.10.2.5 The documentation must be made available to USEPA during on-site laboratory evaluations or sent to USEPA upon request of the Contract Laboratory Program Project Officer (CLP PO) or the Organic Program Manager at Analytical Operations/Data Quality Center (AOC).
- 6.10.2.6 **PACKED COLUMNS CANNOT BE USED.**
- 6.10.3 Mass Spectrometer - The mass spectrometer must be capable of scanning from 35 to 500 atomic mass units (amu) every 1 second or less, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode and producing a mass spectrum which meets all the decafluorotriphenylphosphine (DFTPP) GC/MS performance check technical acceptance criteria (Table D-1) when 50 ng of DFTPP is injected through the GC inlet. To ensure sufficient precision of mass spectral data, the MS scan rate must allow acquisition of at least five spectra while a sample compound elutes from the GC. The GC/MS system must be in a room whose atmosphere is demonstrated to be free of all potential contaminants which will interfere with the analysis. The instrument must be vented outside the facility or to a trapping system which prevents the release of contaminants into the instrument room.
- 6.10.4 GC/MS interface - any GC/MS interface which provides acceptable sensitivity at CRQLs. GC/MS interfaces constructed of all-glass or glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane.

- 6.10.5 Data system - a computer system must be interfaced to the mass spectrometer that allows the continuous acquisition and storage on machine-readable media, of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundance versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundance in any EICP between specified time or scan number limits. Also, for the non-target compounds, software must be available that allows for the comparison of sample spectra against reference library spectra. The NIST/EPA/NIH (May 1992 release or later) and/or Wiley (1991 release or later), or equivalent mass spectral library shall be used as the reference library. The operational data system must be able to flag all data files that have been edited manually by laboratory personnel.
- 6.10.6 Magnetic tape storage device - must be capable of recording data and suitable for long-term, off-line storage of GC/MS data.

Exhibit D Semivolatiles -- Section 7  
Reagents and Standards

7.0 REAGENTS AND STANDARDS

7.1 Reagents

Reagents shall be dated with the receipt date and used on a first-in, first-out basis. The purity of the reagents shall be verified before use.

- 7.1.1 Reagent water - defined as water in which no semivolatile target compound is observed at or above the Contract Required Quantitation Limit (CRQL) listed in Exhibit C for that compound and in which no non-target compound is observed at or above 10 micrograms per liter ( $\mu\text{g/L}$ ).
- 7.1.1.1 Reagent water may be generated by passing tap water through a carbon filter bed containing about 453 grams (g) (1 lb) of activated carbon (Calgon Corp., Filtrasorb-300 or equivalent).
- 7.1.1.2 Reagent water may be generated using a water purification system (Millipore Super-Q or equivalent).
- 7.1.2 Solvents - Acetone, methanol, methylene chloride, isooctane, 2-propanol, toluene. Pesticide quality or equivalent.
- 7.1.3 Sodium sulfate - (ACS) Granular or powdered, anhydrous (J.T. Baker anhydrous powder, catalog #73898, J.T. Baker anhydrous granular #3375, or equivalent). Purify by heating at  $400^{\circ}\text{C}$  for four hours in a shallow tray, cool in a desiccator, and store in a glass bottle. CAUTION: An open container of sodium sulfate may become contaminated during storage in laboratory.
- 7.1.4 Sulfuric acid solution (1:1) - slowly add 50 milliliters (mL) of concentrated  $\text{H}_2\text{SO}_4$  (Sp. Gr. 1.84; 36N) to 50 mL of reagent water.

7.2 Standards

The Contractor must provide all standard solutions to be used with this contract. These standards may be used only after they have been certified according to the procedure in Exhibit E. The Contractor must be able to verify that the standards are certified. Manufacturer's certificates of analysis must be retained by the Contractor and presented upon request.

7.2.1 Stock Standard Solutions

Stock standard solutions may be purchased or prepared using the following procedure.

- 7.2.1.1 Accurately weigh about 0.0100 g of pure material. Dissolve the material in methylene chloride or another suitable solvent and dilute to volume in a 10 mL volumetric flask. Larger volumes may be used at the convenience of the analyst.
- 7.2.1.2 When compound purity is assayed to be 97 percent or greater, the weight may be used without correction to calculate the concentration of the stock solution. If the compound purity is assayed to be less than 97 percent, the weight must be corrected when calculating the concentration of the stock solution.
- 7.2.1.3 Fresh stock standards must be prepared once every twelve months, or sooner, if standards have degraded or concentrated. Stock standards must be checked for signs of degradation or

concentration just prior to preparing secondary dilution and working standards from them.

## 7.2.2 Secondary Dilution Standards

7.2.2.1 Using stock standards, prepare secondary dilution standards in methylene chloride that contain the compounds of interest either singly or mixed together.

7.2.2.2 Fresh secondary dilution standards must be prepared once every twelve months, or sooner, if standards have degraded or concentrated. Secondary dilution standards must be checked for signs of degradation or concentration just prior to preparing working standards from them.

## 7.2.3 Working Standards

### 7.2.3.1 Deuterated Monitoring Compound (DMC) Standard Spiking Solution

7.2.3.1.1 Prepare a DMC standard spiking solution that contains the following compounds at concentrations shown in methanol:

<u>DMC</u>	<u>Concentration</u> <u>: g/mL</u>
Phenol-d5	40
bis-(2-Chloroethyl)ether-d8	40
2-Chlorophenol-d4	40
4-Methylphenol-d8	40
Nitrobenzene-d5	40
2-Nitrophenol-d4	40
2,4-Dichlorophenol-d3	40
4-Chloroaniline-d4	40
Dimethylphthalate-d6	40
Acenaphthylene-d8	40
4-Nitrophenol-d4	40
Fluorene-d10	40
4,6-Dinitro-methylphenol-d2	40
Anthracene-d10	40
Pyrene-d10	40
Benzo(a)pyrene-d12	40

7.2.3.1.2 DMC standards are added to all samples, blanks, requested Matrix Spike/Matrix Spike Duplicate(s) (MS/MSD), and calibration solutions. The DMC standard spiking solution must be prepared every twelve months or sooner if the solution has degraded or concentrated.

### 7.2.3.2 Matrix Spiking Solution

7.2.3.2.1 The matrix spiking solution consists of the following:

<u>Bases/Neutrals</u>	<u>Acids</u>
Acenaphthene	Pentachlorophenol
2,4-Dinitrotoluene	Phenol
Pyrene	2-Chlorophenol
N-Nitroso-di-n-propylamine	4-Chloro-3-methylphenol
	4-Nitrophenol

7.2.3.2.2 Prepare a spiking solution that contains each of the base/neutral compounds above at 20 micrograms per milliliter (:g/mL) in methanol and the acid compounds at 80 :g/mL in methanol.

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7.2.3.2.3           The matrix spiking solution must be prepared every twelve months or sooner if the solution has degraded or concentrated.

7.2.3.3           Instrument Performance Check Solution--DFTPP

Prepare a 50 nanograms per microliter (ng/μL) solution of decafluorotriphenylphosphine (DFTPP) in methylene chloride. The DFTPP solution must be prepared fresh once every twelve months or sooner if the solution has degraded or concentrated.

7.2.3.4           Initial and Continuing Calibration Solutions

7.2.3.4.1           Five initial calibration standard solutions are required for all target compounds and DMCs. Standard concentrations of 5, 10, 20, 50, and 80 ng/μL are required for the DMCs and all but seven of the target compounds. The seven compounds: 2,4-dinitrophenol, 2,4,5-trichlorophenol, 2-nitroaniline, 3-nitroaniline, 4-nitroaniline, 4-nitrophenol, and 4,6-dinitro-2-methylphenol require calibration at 20, 50, 80, 100, and 120 ng/μL.

7.2.3.4.2           To prepare a calibration standard solution, add an appropriate volume of secondary dilution standard to methylene chloride in a volumetric flask. Dilute to volume with methylene chloride.

7.2.3.4.3           The 20 ng/μL initial calibration solution (80 ng/μL for the seven compounds listed in Section 7.2.3.4.1) is the continuing calibration solution.

7.2.3.4.4           The five initial calibration solutions must be prepared fresh before use. The continuing calibration standard solution must be prepared weekly or sooner if the solution has degraded or concentrated.

7.2.3.5           Internal Standard Spiking Solution

7.2.3.5.1           Prepare an internal standard spiking solution in methylene chloride or another suitable solvent that contains 1,4-dichlorobenzene-d<sub>4</sub>, naphthalene-d<sub>8</sub>, acenaphthene-d<sub>10</sub>, phenanthrene-d<sub>10</sub>, chrysene-d<sub>12</sub>, and perylene-d<sub>12</sub> at 2000 ng/μL. It may be necessary to use 5 to 10 percent toluene in this solution and a few minutes of ultrasonic mixing in order to dissolve all the constituents.

NOTE: For automated systems using an injection volume of less than 10 μL, the internal standard solution may need to be prepared at a different concentration.

7.2.3.5.2           The internal standard spiking solution must be prepared every twelve months or sooner if the solution has degraded or concentrated.

7.2.4           Ampulated Standard Extracts

Standard solutions purchased from a chemical supply house as ampulated extracts in glass vials may be retained and used until the expiration date provided by the manufacturer. If no manufacturer's expiration date is provided, the standard solutions as ampulated extracts may be retained and used for 2 years from the preparation date. Standard solutions prepared by the Contractor which are immediately ampulated in glass vials may be retained for 2 years from preparation date. Upon breaking the glass seal, the expiration times



listed in Sections 7.2.1 to 7.2.3.5 will apply. The Contractor is responsible for assuring that the integrity of the standards has not degraded (Section 7.2.5.5).

7.2.5 Storage of Standard Solutions

- 7.2.5.1 Store the stock and secondary standard solutions at 4°C (±2°C) in PTFE-lined screw-cap amber bottles.
- 7.2.5.2 Store the working standard solutions at 4°C (±2°C) in PTFE-lined screw-cap amber bottles.
- 7.2.5.3 Protect all standards from light.
- 7.2.5.4 Samples, sample extracts, and standards must be stored separately.
- 7.2.5.5 The Contractor is responsible for maintaining the integrity of standard solutions and verifying prior to use. Storage of standard solutions in the freezer may cause some compounds to precipitate. This means at the minimum, the standards must be brought to room temperature prior to use, checked for losses, and checked that all components have remained in solution. Additional steps may be necessary to ensure all components are in solution.

7.2.6 Temperature Records for Storage of Standards

- 7.2.6.1 The temperature of all standard storage refrigerators shall be recorded daily.
- 7.2.6.2 Temperature excursions shall be noted and appropriate corrective actions shall be taken to correct problems, when required.
- 7.2.6.3 Corrective action Standard Operating Procedures (SOPs) shall be posted on the refrigerators.

Exhibit D Semivolatiles -- Section 8  
Sample Collection, Preservation and Storage

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Sample Collection and Preservation

8.1.1 Water samples may be collected in 1 liter (L) (or 1 quart) amber glass containers and fitted with screw-caps lined with PTFE. If amber containers are not available, the samples should be protected from light. The specific requirements for site sample collection are outlined by the Region.

8.1.2 All samples must be iced or refrigerated at 4°C (±2°C) from the time of collection until extraction.

8.2 Procedure for Sample Storage

8.2.1 The samples must be protected from light and refrigerated at 4°C (±2°C) from the time of receipt until 60 days after delivery of a complete, reconciled data package to USEPA. After 60 days the samples may be disposed of in a manner that complies with all applicable regulations.

8.2.2 The samples must be stored in an atmosphere demonstrated to be free of all potential contaminants.

8.3 Procedure for Sample Extract Storage

8.3.1 Sample extracts must be protected from light and stored at less than 4°C (±2°C) until 365 days after delivery of a reconciled, complete data package to USEPA.

8.3.2 Samples, sample extracts, and standards must be stored separately.

8.4 Records for Sample and Sample Extract Storage

8.4.1 The temperature of all sample and sample extract storage refrigerators shall be recorded daily.

8.4.2 Temperature excursions shall be noted and appropriate corrective actions shall be taken to correct problems, when required.

8.4.3 Corrective action SOPs shall be posted on the refrigerators.

8.5 Contract Required Holding Times

8.5.1 Extraction of water samples by continuous liquid-liquid procedures shall be started within 5 days of Validated Time of Sample Receipt (VTSR).

NOTE: Separatory funnel extraction procedures are not permitted.

8.5.2 As part of USEPA's QA program, USEPA may provide Performance Evaluation (PE) samples as standard extracts which the Contractor is required to prepare per the instructions provided by USEPA. PE samples must be extracted and analyzed concurrently with the samples in the SDG. The extraction holding time (5 days after VTSR) does not apply to PE samples received as standard extracts.

8.5.3 Extracts of water samples must be analyzed within 40 days following extraction.

9.0 CALIBRATION AND STANDARDIZATION

9.1 Instrument Operating Conditions

9.1.1 Gas Chromatograph (GC)

- 9.1.1.1 The following are the gas chromatographic analytical conditions.  
The conditions are recommended unless otherwise noted.

Initial Column Temperature Hold	40°C for 4 minutes
Column Temperature Program	40-270°C at 10°C/min.
Final Column Temperature Hold	270°C for 3 minutes after all compounds listed in Exhibit C (Semivolatiles) have eluted (required)
Injector Temperature	250-300°C
Transfer Line Temperature	250-300°C
Source Temperature	According to manufacturer's specifications
Injector	Grob-type, splitless
Sample Volume	1 : L
Carrier Gas	Helium at 30 cm/sec

- 9.1.1.2 Optimize GC conditions for analyte separation and sensitivity.  
Once optimized, the same GC conditions must be used for the  
analysis of all standards, samples, blanks, matrix spikes, and  
matrix spike duplicates, if required.

9.1.2 Mass Spectrometer (MS)

The following are the required mass spectrometer analytical  
conditions:

Electron Energy	70 volts (nominal)
Mass Range	35 to 500 amu
Scan Time	Not to exceed 1 second per scan
Ionization Mode	EI

9.2 Instrument Performance Check (DFTPP)

9.2.1 Summary of Instrument Performance Check

The GC/MS system must be tuned to meet the manufacturer's  
specifications, using a suitable calibrant such as perfluoro-tri-n-  
butylamine (FC-43) or perfluorokerosene (PFK). The mass calibration  
and resolution of the GC/MS system are verified by the analysis of  
the instrument performance check solution (Section 7.2.3.3). Prior  
to the analysis of any samples (including requested Matrix  
Spike/Matrix Spike Duplicate (MS/MSD) and PE Samples) blanks and  
calibration standards, the Contractor must establish that the GC/MS  
system meets the mass spectral ion abundance criteria for the  
instrument performance check solution containing decafluoro-  
triphenylphosphine (DFTPP).

9.2.2 Frequency of Instrument Performance Check

- 9.2.2.1 The instrument performance check solution must be analyzed once at  
the beginning of each 12-hour period during which samples, blanks  
or standards are analyzed.

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9.2.2.2 The 12-hour time period for a instrument performance check and standards calibration (initial or continuing calibration criteria) begins at the moment of injection of the DFTPP analysis that the laboratory submits as documentation of a compliant instrument performance check. The time period ends after 12-hours have elapsed according to the system clock.

9.2.3 Procedure for Instrument Performance Check

The analysis of the instrument performance check solution may be performed as an injection of up to 50 nanograms (ng) of DFTPP into the GC/MS or by adding 50 ng of DFTPP to a calibration standard (Section 7.2.3.4.3) and analyzing the calibration standard.

9.2.4 Technical Acceptance Criteria for Instrument Performance Check

9.2.4.1 The GC/MS system must be tuned at the frequency described in Section 9.2.2.

9.2.4.2 The abundance criteria listed in Table D-1 must be met for a 50 ng injection of DFTPP. The mass spectrum of DFTPP must be acquired in the following manner: three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan acquired no more than 20 scans prior to the beginning of the elution of DFTPP. Do not subtract part of the DFTPP peak.

NOTE: All subsequent standards, samples, and blanks associated with a DFTPP analysis must use the identical mass spectrometer instrument conditions.

9.2.5 Corrective Action for Instrument Performance Check

9.2.5.1 If the GC/MS performance check technical acceptance criteria are not met, re-tune the GC/MS system. It may be necessary to clean the ion source, clean quadrupoles, or take other actions to achieve the technical acceptance criteria.

9.2.5.2 GC/MS performance check technical acceptance criteria MUST be met before any standards, samples, and required blanks are analyzed. Any standards, samples, and required blanks analyzed when GC/MS performance check technical acceptance criteria have not been met will require re-analysis at no additional cost to USEPA.

9.3 Initial Calibration

9.3.1 Summary of Initial Calibration

Prior to the analysis of samples and required blanks and after GC/MS performance check technical acceptance criteria have been met, each GC/MS system must be initially calibrated at a minimum of five concentrations (Section 7.2.3.4) to determine instrument sensitivity and the linearity of GC/MS response for the semivolatile target and Deuterated Monitoring Compounds (DMCs).

9.3.2 Frequency of Initial Calibration

9.3.2.1 Each GC/MS system must be initially calibrated upon award of the contract, whenever the Contractor takes corrective action which may change or affect the initial calibration criteria (e.g., ion source cleaning or repair, column replacement, etc.), or if the

continuing calibration technical acceptance criteria have not been met.

- 9.3.2.2 If time still remains in the 12-hour time period after meeting the technical acceptance criteria for the initial calibration, samples and blanks may be analyzed. It is not necessary to analyze a continuing calibration standard within this 12-hour time period, if the initial calibration standard that is the same concentration as the continuing calibration standard meets the continuing calibration technical acceptance criteria. Quantitate all sample and blank results against the initial calibration standard that is the same concentration as the continuing calibration standard (Section 7.2.3.4.3). Compare quality control criteria such as internal standard area response change and retention time shift to the initial calibration standard that is the same concentration as the continuing calibration standard.

9.3.3 Procedure for Initial Calibration

- 9.3.3.1 Set-up the GC/MS system per the requirements of Section 9.1.
- 9.3.3.2 All standard/spiking solutions must be allowed to warm to ambient temperature (approximately 1 hour) before preparation or analysis.
- 9.3.3.3 Prepare five calibration standards containing all the semivolatile target and DMCs at the concentrations described in Section 7.2.3.4.1.
- 9.3.3.4 Add 10 microliters (µL) of the internal standard spiking solution (Section 7.2.3.5) to 1.0 milliliters (mL) of each of the five calibration standards for a concentration of 20 nanograms per microliter (ng/µL) for each internal standard compound.
- 9.3.3.5 Tune the GC/MS system to meet the technical acceptance criteria in Section 9.2.4 for DFTPP.
- 9.3.3.6 Analyze each calibration standard by injecting 1.0 µL of standard.

9.3.4 Calculations for Initial Calibrations

- 9.3.4.1 Calculate Relative Response Factors (RRF) for each semivolatile target compound and DMC using Equation 1. See Table D-2 to associate semivolatile target and deuterated monitoring compounds with the proper internal standard. See Table D-3 for primary quantitation ions to be used for each semivolatile target compound, DMC, and internal standard.

NOTE: Unless otherwise stated the area response is that of the primary quantitation ion.

EQ. 1

$$RRF = \frac{A_x}{A_{is}} \times \frac{C_{is}}{C_x}$$

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Where:

$A_x$  = Area of the characteristic ion for the compound to be measured.

$A_{is}$  = Area of the characteristic ion for the specific internal standard (Table D-2).

$C_{is}$  = Amount of the internal standard injected ( $\mu\text{g}$ ).

$C_x$  = Amount of the compound to be measured injected ( $\mu\text{g}$ ).

9.3.4.2 Calculate the mean Relative Response Factor for each compound using Equation 2.

EQ. 2

$$\bar{x} = \frac{\sum_{i=1}^n x_i}{n}$$

Where:

$x_i$  = Each individual value.

$\bar{x}$  = The mean of  $n$  values.

$n$  = The total number of values.

9.3.4.3 Calculate the percent relative standard deviation (%RSD) of Relative Response Factor (RRF) values for each semivolatile target compound and DMC over the initial calibration range using Equation 3 in conjunction with Equation 4.

EQ. 3

$$\%RSD = \frac{(\text{Standard Deviation})}{\text{Mean}} \times 100$$

Where:

%RSD = Percent relative standard deviation.

9.3.4.4 Equation 4 is the general formula for standard deviation for a statistically small set of values.

EQ. 4

$$\text{Standard Deviation} = \sqrt{\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n-1}}$$

Where:

$x_i$ , 0 and n are as defined in Equation 2.

9.3.5 Technical Acceptance Criteria for Initial Calibration

- 9.3.5.1 All initial calibration standards must be analyzed at the concentration levels described in Section 7.2.3.4.1 and at the frequency described in Section 9.3.2 on a GC/MS system meeting the DFTPP technical acceptance criteria.
- 9.3.5.2 The relative response factor ( $RRF_i$ ) at each calibration concentration for each semivolatile target compound and DMC must be greater than or equal to the compound's minimum acceptable relative response factor listed in Table D-4.
- 9.3.5.3 The %RSD over the initial calibration range for relative response factor for each semivolatile target compound that has a required %RSD must be less than or equal to the %RSD listed in Table D-4.
- 9.3.5.4 Up to four compounds may fail the criteria listed in Sections 9.3.5.2 and 9.3.5.3 and still meet the minimum RRF and %RSD requirements. However, these four compounds must have a minimum RRF greater than 0.010 and %RSD less than or equal to 40.0%.
- 9.3.5.5 Excluding those ions in the solvent front, no quantitation ion may saturate the detector. Consult the manufacturer's instrument manual to determine how saturation is indicated for your instrument.

9.3.6 Corrective Action for Initial Calibrations

- 9.3.6.1 If the technical acceptance criteria for initial calibration are not met, inspect the system for problems. It may be necessary to clean the ion source, change the column, or take other corrective actions to achieve the technical acceptance criteria.
- 9.3.6.2 Initial calibration technical acceptance criteria MUST be met before any samples or required blanks are analyzed. Any samples or required blanks analyzed when initial calibration technical acceptance criteria have not been met will require re-analysis at no additional cost to USEPA.

9.4 Continuing Calibration

9.4.1 Summary of Continuing Calibration

Prior to the analysis of samples and required blanks and after GC/MS performance check technical acceptance criteria and initial calibration technical acceptance criteria have been met, each GC/MS system must be routinely checked by analyzing a continuing calibration standard to ensure that the instrument continues to meet the instrument sensitivity and linearity requirements of the method. The continuing calibration standard contains all the semivolatile target compounds, DMCs, and internal standards.

9.4.2 Frequency of Continuing Calibration

- 9.4.2.1 Each GC/MS used for analysis must be calibrated once every twelve (12) hour time period of operation. The 12-hour time period begins with the injection of DFTPP.

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9.4.2.2 If time still remains in the 12-hour time period after meeting the technical acceptance criteria for the initial calibration, samples and blanks may be analyzed. It is not necessary to analyze a continuing calibration standard within this 12-hour time period, if the initial calibration standard that is the same concentration as the continuing calibration standard meets the continuing calibration technical acceptance criteria. Quantitate all sample and blank results against the 20 ng/μL (80 ng/μL for the seven compounds listed in Section 7.2.3.4.1) calibration standard.

9.4.3 Procedure for Continuing Calibration

9.4.3.1 All standard/spiking solutions must be allowed to warm to ambient temperature (approximately 1 hour) before preparation or analysis.

9.4.3.2 Add 10 μL of the internal standard solution (Section 7.2.3.5) to 1.0 mL of the continuing calibration standard (Section 7.2.3.4.3) for a concentration of 20 ng/μL for each internal standard compound.

9.4.3.3 Analyze the continuing calibration standard by injecting 1.0 μL of standard.

9.4.4 Calculations for Continuing Calibration

9.4.4.1 Calculate a RRF for each semivolatile target compound and DMC using Equation 1 for the primary characteristic ions found in Table D-3.

9.4.4.2 Calculate the percent difference between the mean relative response factor from the most recent initial calibration and the continuing calibration relative response factor for each semivolatile target compound and DMC using Equation 5. For internal standards, use the primary ions listed in Table D-3 unless interferences are present. If interferences prevent the use of the primary ion for a given internal standard, use the secondary ion(s) listed in Table D-3.

EQ. 5

$$\text{Difference}_{\text{RRF}} = \frac{\text{RRF}_c - \text{RRF}_i}{\text{RRF}_i} \times 100$$

Where:

\_\_\_\_\_  
RRF<sub>i</sub> = Mean relative response factor from the most recent initial calibration meeting technical acceptance criteria.

RRF<sub>c</sub> = Relative response factor from continuing calibration standard.

9.4.5 Technical Acceptance Criteria for Continuing Calibration

9.4.5.1 The continuing calibration standard must be analyzed at the 20 ng/μL (80 ng/μL for the seven compounds listed in 7.2.3.4.1) concentration level, and at the frequency described in Section 9.4.2, on a GC/MS system meeting the DFTPP and the initial calibration technical acceptance criteria.



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- 9.4.5.2 The relative response factor for each semivolatile target compound and DMC must be greater than or equal to the compound's minimum acceptable relative response factor listed in Table D-4.
- 9.4.5.3 The relative response factor percent difference for each semivolatile target compound that has a percent difference criteria must be within the inclusive range listed in Table D-4.
- 9.4.5.4 Up to four compounds may fail the requirements listed in Sections 9.4.5.2 and 9.4.5.3 and still meet the minimum relative response factor and percent difference criteria. However, these compounds must have a minimum relative response factor greater than or equal to 0.010 and the percent difference must be within the inclusive range of  $\pm 40\%$ .
- 9.4.5.6 Excluding those ions in the solvent front, no quantitation ion may saturate the detector. Consult the manufacturer's instrument operating manual to determine how saturation is indicated for your instrument.
- 9.4.6 Corrective Action for Continuing Calibration
  - 9.4.6.1 If the continuing calibration technical acceptance criteria are not met, recalibrate the GC/MS instrument according to Section 9.3.3. It may be necessary to clean the ion source, change the column, or take other corrective actions to achieve the technical acceptance criteria.
  - 9.4.6.2 Continuing calibration technical acceptance criteria MUST be met before any samples (including requested MS/MSD) or required blanks are analyzed. Any samples or required blanks analyzed when continuing calibration criteria have not been met will require re-analysis at no additional cost to USEPA.

Exhibit D Semivolatiles -- Section 10  
Procedure

10.0 PROCEDURE

10.1 Sample Preparation

10.1.1 This method is designed for analysis of water samples that contain low concentrations of the semivolatile compounds listed in Exhibit C. The majority of the samples are expected to come from drinking water and well/ground water type sources around Superfund sites. If, upon inspection of a sample, the Contractor suspects that the sample is not amenable to this method, contact Sample Management Office (SMO). SMO will contact the Region for instructions.

10.1.2 If insufficient sample volume (less than 90 percent of the required amount) is received to perform the analyses, the Contractor shall contact SMO to apprise them of the problem. SMO will contact the Region for instructions. The Region will either require that no sample analyses be performed or will require that a reduced volume be used for the sample analysis. No other changes in the analyses will be permitted. The Contractor shall document the Region's decision in the Sample Delivery Group (SDG) Narrative.

10.1.3 Extraction of Sample

10.1.3.1 Allow the sample to come to ambient temperature (approximately 1 hour).

10.1.3.2 Continuous liquid-liquid extraction is used to extract the samples. Separatory funnel extraction cannot be used.

10.1.3.3 Continuous Liquid-Liquid Extraction Without Hydrophobic Membrane

10.1.3.3.1 Follow manufacturer's instructions for set-up.

10.1.3.3.2 Add methylene chloride to the bottom of the extractor and fill it to a depth of at least one inch above the bottom sidearm.

10.1.3.3.3 Measure out a 1 L sample aliquot in a separate, clean graduated cylinder; transfer the aliquot to the continuous extractor. Measure and record the initial pH of the sample with a pH meter or narrow range pH paper. Adjust the pH to 2.0 with 1:1 H<sub>2</sub>SO<sub>4</sub> and record the final pH.

NOTE: With some samples, it may be necessary to place a layer of glass wool between the methylene chloride and the water layer in the extractor to prevent precipitation of suspended solids into the methylene chloride during extraction.

10.1.3.3.4 Using a syringe or volumetric pipet, add 1.0 mL of the Deuterated Monitoring Compound (DMC) standard spiking solution (Section 7.2.3.1) into the sample and mix well.

10.1.3.3.5 Rinse the graduated cylinder with 50 mL of methylene chloride and transfer the rinsate to the continuous extractor. If the sample container is empty, rinse the container with 50 mL of methylene chloride and add rinsate to the continuous extractor.

10.1.3.3.6 Add sufficient methylene chloride to the continuous extractor to ensure proper solvent cycling during operation. Adjust the drip rate to 5 to 15 mL/minute (recommended); optimize the extraction drip rate. Extract for a minimum of 18 hours.

NOTE 1: When a minimum drip rate of 10-15 mLs/min. is maintained throughout the extraction, the extraction time may be reduced to a minimum of twelve hours. Allow to cool, then detach the distillation flask. Proceed to Section 10.1.4.

NOTE 2: Some continuous liquid-liquid extractors are also capable of concentrating the extract within the extraction set-up. Follow the manufacturer's instructions for concentration when using this type of extractor.

10.1.3.4 Continuous Liquid-Liquid Extraction With Hydrophobic Membrane

10.1.3.4.1 Follow the manufacturer's instructions for set-up.

10.1.3.4.2 Measure out each 1 L sample aliquot in a separate, clean graduated cylinder. If the sample container is empty, rinse the container with 50 mL of methylene chloride and add the rinsate to the continuous extractor. If the sample container is not empty, add 50 mL of methylene chloride to the continuous extractor. Slowly transfer the aliquot to the continuous extractor. Measure and record the initial pH of the sample with a pH meter or a narrow range pH paper. Adjust the pH to 2.0 with 1:1 H<sub>2</sub>SO<sub>4</sub> and record the final pH.

10.1.3.4.3 Using a syringe or volumetric pipet, add 1.0 mL of the DMC standard spiking solution (Section 7.2.3.1) into the sample and mix well.

10.1.3.4.4 Rinse the graduated cylinder with 50 mL of methylene chloride and transfer the rinsate to the continuous extractor.

10.1.3.4.5 Add sufficient methylene chloride to the continuous extractor to ensure proper solvent cycling during operation. Adjust the drip rate to 15 mL/minute (recommended); optimize the extraction drip rate. Extract for a minimum of 6 hours.

NOTE 1: Due to the smaller volume of solvent used during the extraction process, some sample matrices (e.g., oily samples, samples containing a high concentration of surfactants) may create an emulsion which will consume the solvent volume, preventing the efficient extraction of the sample. When this occurs, add additional solvent to assure efficient extraction of the sample, and extend the extraction time for a minimum of 6 hours. If the sample matrix prevents the free flow of solvent through the membrane, then the non-hydrophobic membrane continuous liquid-liquid type extractor must be used.

Allow to cool, then detach the distillation flask. Proceed to Section 10.1.4.

NOTE 2: Some continuous liquid-liquid extractors are also capable of concentrating the extract within the extraction set-up. Follow the manufacturer's instructions for concentration when using this type of extractor. Using the hydrophobic membrane type extractor, it may not be necessary to dry the extract with sodium sulfate.

NOTE 3: If low DMC recoveries occur, assure 1) the apparatus was properly assembled to prevent leaks; 2) the drip rate/solvent cycling was optimized; and 3) there was proper cooling for condensation of solvent.

NOTE 4: Alternate continuous liquid-liquid extractor types that meet the requirements of the SOW may also be used. If using alternate extractors or design types, follow the manufacturer's instructions for set-up.

10.1.4 Concentrating the Sample Extract

10.1.4.1 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10 mL concentrator tube to a 500 mL evaporative flask. Other concentration devices or techniques may be used in place of the K-D, if equivalency is demonstrated for all the semivolatile target compounds listed in Exhibit C.

10.1.4.2 Transfer the extract by pouring the extract through a drying column containing about 10 cm of anhydrous granular sodium sulfate, and collect the extract in a K-D concentrator. Rinse the distilling flask and column with 20 to 30 mL of methylene chloride to complete the quantitative transfer.

10.1.4.3 Add one or two clean boiling chips and attach a three-ball Snyder column to the evaporative flask. Pre-wet the Snyder column by adding about 1 mL methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (60°C to 80°C recommended) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 10 to 15 minutes. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. DO NOT ALLOW THE EVAPORATIVE FLASK TO GO DRY. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of methylene chloride. A 5 mL syringe is recommended for this operation.

10.1.4.4 Two different types of concentration techniques are permitted to obtain the final 1.0 mL volume: micro Snyder column and nitrogen evaporation techniques.

10.1.4.4.1 Micro Snyder Column Technique

Add another one or two clean boiling chips to the concentrator tube and attach a two-ball micro Snyder column. Pre-wet the Snyder column by adding about 0.5 mL of methylene chloride to the top of the column. Place the K-D apparatus in a hot water bath (60°C to 80°C recommended) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5 to 10 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches about 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain for at least 10 minutes while cooling. DO NOT LET THE EXTRACT GO DRY. Remove the Snyder column and rinse the evaporative flask and its lower joint into the concentrator tube with 0.2 mL of methylene chloride. Adjust the final volume to 1.0 mL with methylene chloride. Transfer the extract to a PTFE-sealed screw-cap bottle, label the bottle and store at 4°C ( $\pm 2^\circ\text{C}$ ).

10.1.4.4.2 Nitrogen Evaporation Technique (taken from ASTM Method D3086)

Place the concentrator tube in a warm water bath (30°C to 35°C) and evaporate the solvent volume to just below 1 mL by blowing a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon) above the extract. Caution: Gas lines from the gas source to the evaporation apparatus must be stainless steel, copper, or PTFE tubing. New plastic tubing must not be used between the carbon trap and the sample since it may introduce interferences. The internal wall of the concentrator tube must be rinsed down several times with methylene chloride during the operation and the final volume brought to 1.0 mL with methylene chloride. During evaporation, the tube solvent level must be kept below the water level of the bath. The extract must never be allowed to become dry. Transfer the extract to a PTFE-sealed screw-cap bottle, label the bottle and store at 4°C (±2°C).

10.2 Instrument Analysis of Sample

10.2.1 Set up the Gas Chromatograph/ Mass Spectrometer (GC/MS) system per the requirements of Section 9.1. Before samples or required blanks can be analyzed, the instrument must meet the decafluoro-triphenylphosphine (DFTPP), initial calibration, and continuing calibration technical acceptance criteria. All sample, blank extracts, and standard/spiking solutions must be allowed to warm to ambient temperature (approximately 1 hour) before analysis. All sample extracts [including requested Matrix Spike/Matrix Spike Duplicate (MS/MSD)] and required blanks must be analyzed under the same instrumental conditions as the calibration standards.

10.2.2 Add 10.0 µL of the internal standard spiking solution (Section 7.2.3.5) to the 1.0 mL extract. For sample dilutions, add an appropriate amount of the internal standard spiking solution to maintain a 20 nanograms per microliter (ng/µL) concentration of the internal standards in the diluted extract.

NOTE: An alternate amount of internal standard solution may be added, however the internal standards must be added to maintain the required 20 ng/µL of each internal standard in the sample extract.

10.2.3 Inject 1.0 µL of sample extract into the GC/MS, and start data acquisition.

10.2.4 Three minutes after all semivolatile target compounds have eluted from the GC, terminate the MS data acquisition and store data files on the data system storage device. Use appropriate data output software to display full range mass spectra and Extracted Ion Current Profiles (EICPs).

10.2.5 Sample Dilutions

An original undiluted analysis must be made and results reported for all samples.

10.2.5.1 When a sample extract is analyzed that has a semivolatile target compound concentration greater than the upper limit of the initial calibration range or in which ions from a target compound saturate the detector (excluding the compound peaks in the solvent front), the extract must be diluted, the internal standard concentration must be readjusted, and the sample extract must be re-analyzed. Secondary ion quantitation is only allowed when there are sample

interferences with the primary quantitation ion, not when saturation occurs. If secondary ion quantitation is used, calculate a relative response factor using the area response (EICP) from the most intense secondary ion which is free of sample interferences, and document the reasons for the use of the secondary ion in the SDG Narrative.

NOTE: If the laboratory has evidence or highly suspects, because of sample color or other physical property, that a sample may contain extremely high concentrations of either target or non-target compounds, then SMO shall be immediately contacted. SMO will seek regional recommendations for diluted analysis.

- 10.2.5.2 Dilute the sample using the following procedure:
  - 10.2.5.2.1 Calculate the sample dilution necessary to keep the semivolatile target compounds that required dilution above the mid-point standard in the initial calibration range and so that no target compound has ions which saturate the detector (excluding the compound peaks in the solvent front).
  - 10.2.5.2.2 Dilute the sample extract quantitatively with methylene chloride.
  - 10.2.5.2.3 Analyze the sample dilution per Section 10.2, including the addition of internal standards to maintain a 20 ng/ $\mu$ L concentration of the internal standards (Section 10.2.2).

## 11.0 DATA ANALYSIS AND CALCULATIONS

### 11.1 Qualitative Identification of Target Compounds

- 11.1.1 The compounds listed in the Target Compound List (TCL), Exhibit C, shall be identified by an analyst competent in the interpretation of mass spectra by comparison of the sample mass spectrum to the mass spectrum of a standard of the suspected compound. Two criteria must be satisfied to verify the identifications.
- Elution of the sample analyte within Gas Chromatograph (GC) Relative Retention Time (RRT) unit window established from the 12-hour calibration standard.
  - Correspondence of the sample analyte and calibration standard component mass spectra.
- 11.1.2 For establishing correspondence of the GC RRT, the sample component RRT must be within  $\pm 0.06$  RRT units of the RRT of the standard component. For reference, the standard must be run on the same shift as the sample. For samples analyzed during the same 12-hour time period as the initial calibration standards, compare the analyte retention times to those from the 20 nanograms per microliter (ng/ $\mu$ L) (80 ng/ $\mu$ L for the seven compounds listed in Section 7.2.3.4.1) calibration standard. If coelution of interfering compounds prohibits accurate assignment of the sample component RRT from the Extracted Ion Current Profile (EICP) for the primary ion, the RRT must be assigned by using the total ion chromatogram.
- 11.1.3 For comparison of standard and sample component mass spectra, mass spectra obtained on the Contractor's GC/MS are required. These standard spectra may be used for identification purposes only if the Contractor's GC/MS meets the decafluorotriphenylphosphine (DFTPP) technical acceptance criteria. These standard spectra may be obtained from the analysis used to obtain reference RRTs.
- 11.1.4 The requirements for qualitative verification by comparison of mass spectra are as follows:
- 11.1.4.1 All ions present in the standard mass spectra at a relative intensity greater than 10 percent (most abundant ion in the spectrum equals 100 percent) must be present in the sample spectrum.
- 11.1.4.2 The relative intensities of the major ions specified in Section 11.1.4.1 must agree within  $\pm 20$  percent between the standard and sample spectra. (Example: For an ion with an abundance of 50 percent in the standard spectra, the corresponding sample ion abundance must be between 30 and 70 percent.)
- 11.1.4.3 Ions greater than 10 percent in the sample spectrum but not present in the standard spectrum must be considered and accounted for by the analyst making the comparison. The verification process should FAVOR FALSE POSITIVES. All compounds meeting the identification criteria must be reported with their spectra. When target compounds are below Contract Required Quantitation Limits (CRQLs) but the spectrum meets the identification criteria, report the concentration with a "J". For example, if the CRQL is 5.0 micrograms per liter ( $\mu$ g/L) and a concentration of 3.0  $\mu$ g/L is calculated, report the data as "3.0J".

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11.1.5 If a compound cannot be verified by all of the criteria in Sections 11.1.1 through 11.1.4, but in the technical judgment of the mass spectral interpretation specialist, the identification is correct, then the Contractor shall report that identification and proceed with quantitation.

11.2 Qualitative Identification of Non-Target Compounds

11.2.1 A library search shall be executed for non-target compounds for the purpose of tentative identification. The NIST/EPA/NIH (May 1992 release or later) and/or Wiley (1991 release or later), or equivalent mass spectral library shall be used as the reference library (Section 6.10.5).

11.2.2 Up to 30 non-DMC/non-internal standard organic compounds of greatest apparent concentration not listed in Exhibit C for the volatiles and semivolatiles shall be tentatively identified via a forward search of the NIST/EPA/NIH and/or Wiley mass spectral library, or equivalent mass spectral library. The following are not to be reported:

- Compounds with responses less than 10 percent of the internal standard (as determined by inspection of peak areas or heights);
- Compounds which elute earlier than 30 seconds before the first semivolatile compound listed in Exhibit C (Semivolatiles) or three minutes after the last semivolatile compound listed in Exhibit C (Semivolatile) has eluted; and
- Volatile compounds listed in Exhibit C. Only after visual comparison of sample spectra to spectra resulting from the library search(es) will the mass spectral interpretation specialist assign a tentative identification.

NOTE: Computer generated library search routines must not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

11.2.3 Up to 20 peaks of greatest apparent concentration (as determined by inspection of peak areas or heights) that are suspected to be straight-chain, branched, or cyclic alkanes, alone or part of an alkane series shall be library searched. When the above alkanes are tentatively identified, the concentration(s) are to be estimated as described in Section 11.4 and reported in the SDG Narrative as alkanes, by class (i.e., straight chain, branched, or cyclic; as a series; as applicable). Alkanes are not counted as part of the 30 organic compounds described in Section 11.2.2.

11.2.4 Peaks that are suspected to be aldol-condensation reaction products (e.g., 4-methyl-4-hydroxy-2-pentanone and 4-methyl-3-pentene-2-one) shall be searched, reported, and counted as part of the 30 most intense non-target semivolatile compounds, and qualified with an "A" flag on Form I LCSV-TIC.

11.2.5 Guidelines for making Tentative Identification

11.2.5.1 Major ions in the reference spectrum (ions greater than 10 percent of the most abundant ion) should be present in the sample spectrum.

11.2.5.2 The relative intensities of the major ions should agree within  $\pm 20$  percent. (Example: For an ion with an abundance of 50 percent in



the standard spectra, the corresponding sample ion abundance should be between 30 and 70 percent.)

- 11.2.5.3 Molecular ions present in reference spectrum should be present in sample spectrum.
- 11.2.5.4 Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.
- 11.2.5.5 Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting compounds.  
  
NOTE: Data system library reduction programs can sometimes create these discrepancies.
- 11.2.5.6 Non-target compounds receiving a library search match of 85% or higher should be considered a "probable match". The compound should be reported unless the mass spectral interpretation specialist feels there is just evidence not to report the compound as identified by the library search program. The lab should include in the SDG Narrative the justification for not reporting a compound as listed by the search program.
- 11.2.5.7 If the library search produces more than one compound at or above 85%, report the compound with the highest percent match (report first compound if percent match is the same for two or more compounds), unless the mass spectral interpretation specialist feels that the highest match compound should not be reported, or another compound with a lower match should be reported. The lab should include in the Sample Delivery Group (SDG) Narrative the justification for not reporting the compound with the highest spectral match.
- 11.2.5.8 If the library search produces a series of obvious isomer compounds with library search matches greater than 85% (e.g., tetramethyl naphthalenes), the compound with the highest library search percent match should be reported (or first compound if library search matches are the same). A note should be placed in the SDG Narrative indicating the exact isomer configuration as reported may not be accurate.
- 11.2.5.9 If library search matches of less than 85% are produced and in the technical judgement of the mass spectral interpretation specialist, no valid tentative identification can be made, the compound should be reported as unknown. The mass spectral specialist should give additional classification of the unknown compound, if possible (e.g., unknown phthalate, unknown hydrocarbon, unknown acid type, unknown chlorinated compound). If a probable molecular weight can be distinguished, include it.
- 11.2.5.10 The Contractor shall report pesticide target compounds listed in Exhibit C (Pesticides) that appear as semivolatile tentatively identified compounds.

### 11.3 Calculations for Target Compounds

- 11.3.1 Target compounds identified shall be quantitated by the internal standard method. The internal standard used shall be the one assigned to that analyte for quantitation (Table D-2). The Relative

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Response Factor (RRF) from the continuing calibration analysis is used to calculate the concentration in the sample. For samples analyzed during the same 12-hour time period as the initial calibration standards, use the RRF values from the mid-point initial calibration standard.

- 11.3.2 Secondary ion quantitation is allowed only when there are sample interferences with the primary ion. If secondary ion quantitation is performed, document the reason in the SDG Narrative. The area of a secondary ion cannot be used for the area of the primary ion unless a relative response factor is calculated using the secondary ion.

NOTE: Unless otherwise stated, the area response is from the EICP of the primary quantitation ion. The primary quantitation ions for the target compounds, internal standards, and DMCs are listed in Table D-3.

- 11.3.3 Calculate target compound concentrations using Equation 6.

EQ. 6

$$\text{Concentration } \mu\text{g/L} = \frac{(A_x) (I_s) (V_o) (Df)}{(A_{is}) (RRF) (V_o) (V_i)}$$

Where:

- $A_x$  = Area response (EICP) of the characteristic ion for the compound to be measured.
- $A_{is}$  = Area response (EICP) of the characteristic ion for the internal standard. The target compounds are listed with their associated internal standard in Table D-2.
- $I_s$  = Amount of internal standard injected in nanograms (ng).
- RRF = Relative response factor from the most recent continuing calibration as determined in Section 9.4.
- $V_o$  = Volume of water extracted in milliliters (mL).
- $V_i$  = Volume of extract injected in microliters ( $\mu\text{L}$ ).
- $V_t$  = Volume of concentrated extract in microliters ( $\mu\text{L}$ ).  
( $V_t = 1000 \mu\text{L}$ )
- Df = Dilution Factor. The dilution factor for analysis of water samples for semivolatiles by this method is defined as follows:

$$\frac{\mu\text{L most conc. extract used to make dilution} + \mu\text{L clean solvent}}{\mu\text{L most conc. extract used to make dilution}}$$

If no dilution is performed, Df = 1.0.

- 11.3.4 When a target compound concentration is below the CRQL, but the spectra meet the identification criteria, report the concentration with a "J". For example, if the CRQL is 5.0  $\mu\text{g/L}$  and a concentration of 3.0  $\mu\text{g/L}$  is calculated, report as "3.0 J". Report ALL sample concentration data as UNCORRECTED for blanks.

- 11.3.5 Calculate the adjusted CRQL for semivolatile compounds using Equation 7.

NOTE: If the adjusted CRQL is less than the CRQL listed in Exhibit C (Semivolatiles), report the CRQL listed in Exhibit C (Semivolatiles).

EQ. 7

$$\text{Adjusted CRQL} = \text{Contract CRQL} \times \frac{\text{Contract Sample Vol (1000 mL)}}{V_o} \times Df \times \frac{V_t}{\text{Contract Ext. Vol (1000 uL)}} \times \frac{\text{Contract Injection Vol (1 uL)}}{V_i}$$

Where:

Contract CRQL = CRQL values reported in Exhibit C of the SOW.

$V_o$  = Same as EQ. 6.

$V_i$  = Same as EQ. 6.

$V_t$  = Same as EQ. 6.

Df = Same as EQ. 6.

- 11.3.6 It is expected that situations will arise where the automated quantitation procedures in the GC/MS software provide inappropriate quantitations. This normally occurs when there is compound co-elution, baseline noise, or matrix interferences. In these circumstances, the Contractor must perform a manual quantitation. Manual quantitations are performed by integrating the area of the quantitation ion of the compound. This integration shall only include the area attributable to the specific TCL, DMC, or internal standard compound. The area integrated shall not include baseline background noise. The area integrated shall not extend past the point where the sides of the peak intersect with the baseline noise. Manual integration is not to be used solely to meet QC criteria, nor is it to be used as a substitute for corrective action on the chromatographic system. Any instance of manual integration must be documented in the SDG Narrative.

- 11.3.7 In all instances where the data system report has been edited, or where manual integration or quantitation has been performed, the GC/MS operator must identify such edits or manual procedures by initialing and dating the changes made to the report and shall include the integration scan range. In addition, a hardcopy printout of the EICP of the quantitation ion displaying the manual integration shall be included in the raw data. This applies to all compounds listed in Exhibit C (Semivolatiles), internal standards, and DMCs.

- 11.3.8 The requirements listed in 11.3.4 and 11.3.5 apply to all standards, samples [including requested Matrix Spike/Matrix Spike Duplicate (MS/MSD)], and blanks.

- 11.3.9 Internal Standard Responses and Retention Times

Internal standard responses and retention times in all samples and blanks must be evaluated during or immediately after data acquisition. Compare the sample/blank internal standard responses

and retention times to the continuing calibration internal standard responses and retention times. For samples and blanks analyzed during the same 12-hour time period as the initial calibration standards, compare the internal standard responses and retention times against the 20 ng/μL (80 ng/μL for the seven compounds listed in Section 7.2.3.4.1) calibration standard. The EICP of the internal standards must be monitored and evaluated for each sample and blank.

#### 11.4 Calculations for Non-Target Compounds

Equation 6 is used for calculating the concentrations of the non-target compounds. Total area counts (or peak heights) from the Reconstructed Ion Chromatograms (RICs) are to be used for both the non-target compound to be measured ( $A_x$ ) and the internal standard ( $A_{is}$ ). Associate the nearest internal standard free of interferences with the non-target compound to be measured. A RRF of one (1) is to be assumed. The value from this quantitation shall be qualified as "J" (estimated due to lack of a compound-specific relative response factor), and "N" (presumptive evidence of presence), indicating the qualitative and quantitative uncertainties associated with this non-target compound. This estimated concentration must be calculated for all tentatively identified compounds as well as those identified as unknowns.

#### 11.5 Calculations for Deuterated Monitoring Compounds (DMCs)

- 11.5.1 Calculate the concentration of the DMCs using the same equation as used for the target compounds.
- 11.5.2 Calculate the DMC percent recovery in all samples and blanks using Equation 8. Determine if recovery is within limits (Table D-5) and report on appropriate form.

EQ. 8

$$\text{Percent Recovery} = \frac{Q_d}{Q_a} \times 100$$

Where:

$Q_d$  = Concentration or amount determined by analysis.

$Q_a$  = Concentration or amount added to sample/blank.

#### 11.6 Technical Acceptance Criteria for Sample Analysis

- 11.6.1 The sample must be analyzed on a GC/MS system meeting the GC/MS performance check, initial calibration, and continuing calibration technical acceptance criteria.
- 11.6.2 The sample must be extracted and analyzed within the contract holding times.
- 11.6.3 The sample must have an associated method blank meeting the blank technical acceptance criteria.
- 11.6.4 The percent recovery for the DMCs in the sample must be within the acceptance windows listed in Table D-5. Up to four DMCs per sample may fail to meet the recovery limits listed in Table D-5.

NOTE: The DMC recovery requirements do not apply to a sample that has been diluted.

- 11.6.5 The instrumental area response (EICP area) for each of the internal standards in the sample must be within the inclusive range of -50 percent and +100 percent of its response in the most recent continuing calibration standard analysis.
  - 11.6.6 The retention time shift for each of the internal standards in the sample must be within  $\pm 0.33$  minutes (20.0 seconds) of its retention time in the most recent continuing calibration standard analysis.
  - 11.6.7 The RRT of each DMC in the sample must be within  $\pm 0.06$  RRT units of its relative retention time in the most recent continuing calibration standard analysis.
  - 11.6.8 Excluding those ions in the solvent front, no ion may saturate the detector. No target compound concentration may exceed the upper limit of the initial calibration range unless a more dilute aliquot of the sample extract is also analyzed according to the procedures in Section 10.2.5.
- 11.7 Corrective Action for Sample Analysis
- 11.7.1 If the sample technical acceptance criteria for the DMCs and internal standards are not met, check calculations, DMC and internal standard solutions, and instrument performance. It may be necessary to recalibrate the instrument or take other corrective action procedures to meet the DMC and internal standard technical acceptance criteria.
  - 11.7.2 If the Contractor needs to analyze more than one (1) sample dilution other than the original analysis to have all the target compounds within the initial calibration range and to have no ions saturating the detector (excluding the peaks in the solvent front), contact Sample Management Office (SMO). SMO will contact the Region for instructions.
  - 11.7.3 Corrective actions for failure to meet instrument performance checks, initial calibration, continuing calibration and method blanks must be completed before the analysis of samples.
  - 11.7.4 Sample analysis technical acceptance criteria MUST be met before data is reported. Samples contaminated from laboratory sources or associated with a contaminated method blank -- or any samples analyzed not meeting the technical acceptance criteria -- will require re-extraction and/or re-analysis at no additional cost to USEPA.
  - 11.7.5 Sample reruns performed as a result of suspected matrix interferences beyond the scope of the method will be reviewed on a case-by-case basis for payment purposes by the USEPA Contract Laboratory Program Project Officer (CLP PO). Send a copy of the SDG Narrative (including your contract number), a description of the situation, and the requested action to the CLP PO.

Exhibit D Semivolatiles -- Section 12  
Quality Control

12.0 QUALITY CONTROL

12.1 Method Blank

12.1.1 Summary of Method Blank

A method blank is 1.0 liter (L) of reagent water carried through the entire analytical scheme. The purpose of a method blank is to determine the levels of contamination associated with the processing and analysis of samples.

12.1.2 Frequency of Method Blank

12.1.2.1 A method blank must be extracted each time samples are extracted. The number of samples extracted with each method blank shall not exceed 20 field samples (excluding Matrix Spike/Matrix Spike Duplicate(s) MS/MSD, if required, and Performance Evaluation (PE) samples).

12.1.2.2 Each method blank must be analyzed on each Gas Chromatograph/Mass Spectrometer (GC/MS) system used to analyze the samples prepared with the method blank.

12.1.3 Procedure for Method Blank

Measure out 1.0 L of reagent water for each method blank aliquot. Extract, concentrate and analyze the method blank at the same time as the samples associated with the blank according to Section 10.

12.1.4 Calculations for Method Blank

Perform data analysis and calculations according to Section 11.

12.1.5 Technical Acceptance Criteria For Method Blank

12.1.5.1 All blanks must be analyzed at the frequency described in Section 12.1.2 on a GC/MS system meeting the GC/MS performance check, initial calibration, and continuing calibration technical acceptance criteria.

12.1.5.2 The percent recovery for each of the Deuterated Monitoring Compounds (DMCs) in the blank must be within the acceptance windows listed in Table D-5.

12.1.5.3 The area response for each of the internal standards in the blank must be within the inclusive range of -50 percent and +100 percent of its response in the most recent continuing calibration standard analysis.

12.1.5.4 The retention time shift for each of the internal standards in the blank must be within  $\pm 0.33$  minutes (20.0 seconds) of its retention time in the most recent continuing calibration standard analysis.

12.1.5.5 The Relative Retention Time (RRT) of each DMC in the blank must be within  $\pm 0.06$  RRT units of its relative retention time in the most recent continuing calibration standard analysis.

12.1.5.6 The concentration of all target compounds (except the phthalate esters listed in Exhibit C) in the blanks must be less than the Contract Required Quantitation Limit (CRQL) for each target compound. A method blank for semivolatile analysis must contain less than five times (5X) the CRQL of the phthalate esters listed

in Exhibit C. The concentration of non-target compounds in the blanks must not exceed 10 micrograms per liter ( $\mu\text{g/L}$ ).

12.1.6 Corrective Action for Method Blank

- 12.1.6.1 If a Contractor's blank does not meet the technical acceptance criteria for method blanks the Contractor shall consider the analytical system to be out of control.
- 12.1.6.2 It is the Contractor's responsibility to ensure that method interferences caused by contaminants in solvents, reagents, glassware, and sample storage and processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms be eliminated.
- 12.1.6.3 If contamination is a problem, the source of the contamination must be investigated and appropriate corrective measures MUST be taken and documented before further sample analysis proceeds. Further, all samples (including requested MS/MSD and PE samples) processed with a method blank that does not meet the blank technical acceptance criteria (i.e., contaminated) will require re-extraction and re-analysis at no additional cost to USEPA.
- 12.1.6.4 If DMC recoveries in the method blank do not meet the technical acceptance criteria (Section 12.1.5.2), first re-analyze the method blank. If the DMC recoveries do not meet the technical acceptance criteria after re-analysis, then all samples (including requested MS/MSD and PE samples) associated with that method blank must be re-extracted and re-analyzed at no additional cost to USEPA.
- 12.1.6.5 If the method blank fails to meet a technical acceptance criteria other than Sections 12.1.5.6 and 12.1.5.2, then the problem is an instrument problem. Correct the instrument problem, recalibrate the instrument (if necessary), and re-analyze the method blank. Sample analysis cannot proceed until the method blank meets these technical acceptance requirements.

12.2 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

12.2.1 Summary of MS/MSD

In order to evaluate the effects of the sample matrix on the methods used for semivolatile analyses, USEPA has prescribed a mixture of semivolatile target compounds to be spiked into two aliquots of a sample and analyzed in accordance with the appropriate method upon request.

12.2.2 Frequency of MS/MSD Analyses

- 12.2.2.1 A matrix spike and matrix spike duplicate shall only be analyzed if requested by the Region [(through the Sample Management Office (SMO)] or specified on the Traffic Report (TR). If requested, a matrix spike and matrix spike duplicate must be extracted and analyzed for every 20 field samples in a Sample Delivery Group (SDG), or each SDG, whichever is most frequent.
- 12.2.2.2 As part of USEPA's QA/QC program, water rinsate samples and/or field/trip blanks (field QC) may be delivered to the laboratory for analysis. The Contractor shall not perform MS/MSD analysis on any of the field QC samples.

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Quality Control (Con't)

- 12.2.2.3 If the USEPA Region requesting MS/MSD designates a sample to be used as an MS/MSD, then that sample must be used. If there is insufficient sample remaining to perform an MS/MSD, then the Contractor shall choose another sample on which to perform an MS/MSD analysis. At the time the selection is made, the Contractor shall notify the Region (through SMO) that insufficient sample was received and identify the USEPA sample selected for the MS/MSD analysis. The rationale for the choice of another sample other than the one designated by USEPA shall be documented in the SDG Narrative.
- 12.2.2.4 If there is insufficient sample remaining in any of the samples in an SDG to perform the requested MS/MSD, then the Contractor shall immediately contact SMO to inform them of the problem. SMO will contact the Region for instructions. The Region will either approve that no MS/MSD is required, or require that a reduced sample aliquot be used for the MS/MSD analysis. SMO will notify the Contractor of the Region's decision. The Contractor shall document the decision in the SDG Narrative.
- 12.2.2.5 If it appears that the Region has requested MS/MSD analysis at a greater frequency than specified in Section 12.2.2.1, then the Contractor shall contact SMO. SMO will contact the Region to determine which samples should have MS/MSD performed on them. SMO will notify the Contractor of the Region's decision. The Contractor shall document the decision in the SDG Narrative. If this procedure is not followed, the Contractor will not be paid for MS/MSD analysis performed at a greater frequency than required by the contract.
- 12.2.2.6 When a Contractor receives only PE samples, no MS/MSD shall be performed within that SDG.
- 12.2.2.7 When a Contractor receives a performance evaluation (PE) sample as part of a larger SDG, a sample other than the PE sample must be chosen for the requested MS/MSD analysis when the Region did not designate a sample to be used for this purpose.
- 12.2.3 Procedure for Preparing MS/MSD
- 12.2.3.1 Measure out two additional 1 L aliquots of the sample chosen for spiking in two continuous extractors. Add 1.0 mL of DMC spiking solution (Section 7.2.3) and 1.0 mL of the matrix spiking solution (Section 7.2.3.2) to each aliquot. Extract, concentrate, and analyze the MS/MSD according to the procedures described in Section 10.
- 12.2.4 Dilution of MS/MSD
- MS/MSD samples must be analyzed at the same concentration as the most concentrated extract for which the original sample results will be reported. For example, if the original sample is to be reported at a 1:1 dilution and a 1:10 dilution, then analyze and report the MS/MSD at a 1:1 dilution only. However, if the original sample is to be reported at a 1:10 dilution and a 1:100 dilution, then the MS/MSD must be analyzed and reported at a 1:10 dilution only. Do not further dilute the MS/MSD samples to get either spiked or non-spiked analytes within calibration range. Dilution of the sample must be performed in accordance to the conditions in Section 10.2.5.



12.2.5 Calculations for MS/MSD

- 12.2.5.1 Calculate the recovery of each matrix spike compound in the matrix spike and matrix spike duplicate samples and report on the appropriate form. Calculate the concentrations of the matrix spike compounds using the same equation as used for target compounds (Equation 6). Calculate the recovery of each matrix spike compound as follows:

EQ. 9

$$\text{Matrix Spike Recovery} = \frac{\text{SSR} - \text{SR}}{\text{SA}} \times 100$$

Where:

SSR = Spike sample result.

SR = Sample result.

SA = Spike added.

- 12.2.5.2 Calculate the Relative Percent Difference (RPD) of the recoveries of each compound in the matrix spike and matrix spike duplicate as follows:

EQ. 10

$$\text{RPD} = \frac{|\text{MSR} - \text{MSDR}|}{\frac{1}{2} (\text{MSR} + \text{MSDR})} \times 100$$

Where:

MSR = Matrix spike recovery.

MSDR = Matrix spike duplicate recovery.

12.2.6 Technical Acceptance Criteria for MS/MSD

- 12.2.6.1 If requested, all MS/MSD must be prepared and analyzed at the frequency described in Section 12.2.2. All MS/MSD must be analyzed on a GC/MS system meeting decafluorotriphenylphosphine (DFTPP), initial and continuing calibration technical acceptance criteria, and the method blank technical acceptance criteria.
- 12.2.6.2 The MS/MSD must have an associated method blank meeting the blank technical acceptance criteria.
- 12.2.6.3 The MS/MSD must be extracted and analyzed within the contract holding time.
- 12.2.6.4 The retention time shift for each of the internal standards must be within  $\pm 0.33$  minutes (20 seconds) between the MS/MSD sample and the most recent continuing calibration standard.
- 12.2.6.5 The relative retention time for the DMCs must be within  $\pm 0.06$  RRT units of its standard retention time in the continuing calibration standard.

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12.2.6.6 The limits for matrix spike compound recovery and RPD are given in Table D-6. As these limits are only advisory, no further action by the laboratory is required; however, frequent failures to meet the limits for recovery or RPD warrant investigation by the laboratory, and may result in questions from USEPA.

12.2.6.7 Corrective Action for Matrix Spike/Matrix Spike Duplicate (MS/MSD)

Any MS/MSD which fails to meet the technical acceptance criteria in Sections 12.2.6.1 through 12.2.6.5 must be re-analyzed at no additional cost to USEPA.

12.3 Method Detection Limit (MDL) Determination

12.3.1 Before any field samples are analyzed under this contract, the MDL for each semivolatile target compound shall be determined for each sample extraction procedure and on one of the instruments to be used for sample analysis. The MDLs must be verified annually thereafter (see Section 12.3.2 for MDL verification procedures), until the contract expires or is terminated or after major instrument maintenance. Major instrument maintenance includes, but is not limited to cleaning or replacement of the mass spectrometer source, mass filters (e.g., quadrupole, ion trap, etc.), or electron multiplier (or similar device), or replacement of gas chromatographic column.

12.3.2 To determine the MDLs, the Contractor shall run an MDL study following the procedures specified in 40 CFR Part 136. The Contractor is only required to analyze the MDL samples on one instrument used for field sample analyses. MDL verification only is then required on all other instruments used for field sample analysis and at the frequency specified in Section 12.3.1. MDL verification is achieved by analyzing a single reagent water blank spiked with each target compound at a concentration equal to two times the analytical determined MDL. The resulting mass spectra of each target compound must meet the qualitative identification criteria outlined in Sections 11.1.1 through 11.1.4.3.

12.3.3 The determined concentration of the MDL must be less than the CRQL.

12.3.4 All documentation for the MDL studies shall be maintained at the laboratory and provided to USEPA upon written request.

13.0 METHOD PERFORMANCE

Not Applicable.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. USEPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, USEPA recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions, consult Less is Better: Laboratory Chemical Management for Waste Reduction, available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington D.C. 20036, (202) 872-4477.

15.0 WASTE MANAGEMENT

USEPA requires that laboratory waste management practices be conducted consistently with all applicable rules and regulations. USEPA urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management consult The Waste Management Manual for Laboratory Personnel, available from the American Chemical Society at the address listed in Section 14.2.

16.0 REFERENCES

Not Applicable.

17.0 TABLES/DIAGRAMS/FLOWCHARTS

Table D-1

DFTPP KEY IONS AND ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
51	30.0 - 80.0 percent of mass 198
68	Less than 2.0 percent of mass 69
69	Present
70	Less than 2.0 percent of mass 69
127	25.0 - 75.0 percent of mass 198
197	Less than 1.0 percent of mass 198
198	Base peak, 100 percent relative abundance (see note)
199	5.0 - 9.0 percent of mass 198
275	10.0 - 30.0 percent of mass 198
365	Greater than 0.75 percent of mass 198
441	Present but less than mass 443
442	40.0 - 110.0 percent of mass 198
443	15.0 - 24.0 percent of mass 442

NOTE: All ion abundances MUST be normalized to m/z 198, the nominal base peak, even though the ion abundances of m/z 442 may be up to 110 percent that of m/z 198.

Table D-2

Semivolatile Internal Standards With Corresponding  
Target and Deuterated Monitoring Compounds Assigned for Quantitation

1,4-Dichlorobenzene-d <sub>4</sub>	Naphthalene-d <sub>8</sub>	Acenaphthene-d <sub>10</sub>
Benzaldehyde	Nitrobenzene	Hexachlorocyclopentadiene
Phenol	Isophorone	2,4,6-Trichlorophenol
bis(2-Chloroethyl)ether	2-Nitrophenol	2,4,5-Trichlorophenol
2-Chlorophenol	2,4-Dimethylphenol	1,1'-Biphenyl
2-Methylphenol	bis(2-Chloroethoxy)methane	2-Chloronaphthalene
2,2'-oxybis-(1-Chloro-propane)	2,4-Dichlorophenol	2-Nitroaniline
Acetophenone	4-Chloroaniline	Dimethylphthalate
4-Methylphenol	Hexachlorobutadiene	Acenaphthylene
N-Nitroso-Di-n-propylamine	Caprolactam	3-Nitroaniline
Hexachloroethane	4-Chloro-3-methylphenol	Acenaphthene
Phenol-d <sub>5</sub> (DMC)	2-Methylnaphthalene	2,4-Dinitrophenol
Bis(2-chloroethyl)ether-d <sub>8</sub> (DMC)	Naphthalene	4-Nitrophenol
2-Chlorophenol-d <sub>4</sub> (DMC)	Nitrobenzene-d <sub>5</sub> (DMC)	Dibenzofuran
4-Methylphenol-d <sub>8</sub> (DMC)	2-Nitrophenol-d <sub>4</sub> (DMC)	2,4-Dinitrotoluene
	2,4-Dichlorophenol-d <sub>3</sub> (DMC)	2,6-Dinitrotoluene
	4-Chloroaniline-d <sub>4</sub> (DMC)	1,2,4,5-Tetrachlorobenzene
		Diethylphthalate
		4-Chlorophenyl-phenylether
		Fluorene
		4-Nitroaniline
		Acenaphthylene-d <sub>8</sub> (DMC)
		4-Nitrophenol-d <sub>4</sub> (DMC)
		Dimethylphthalate-d <sub>6</sub> (DMC)
		Fluorene-d <sub>10</sub> (DMC)

Exhibit D Semivolatiles -- Section 17  
Tables/Diagrams/Flowcharts (Con't)

Table D-2 (Con't)

Semivolatile Internal Standards With Corresponding  
Target and Deuterated Monitoring Compounds Assigned for Quantitation

Phenanthrene-d <sub>10</sub>	Chrysene-d <sub>12</sub>	Perylene-d <sub>12</sub>
4,6-Dinitro-2-methylphenol	Pyrene	Di-n-octylphthalate
N-nitrosodiphenylamine	Butylbenzylphthalate	Benzo(b)fluoranthene
4-Bromophenyl-phenylether	3,3'-Dichlorobenzidine	Benzo(k)fluoranthene
Hexachlorobenzene	Benzo(a)anthracene	Benzo(a)pyrene
Atrazine	bis(2-Ethylhexyl)phthalate	Indeno(1,2,3-cd)pyrene
Pentachlorophenol	Chrysene	Dibenzo(a,h)anthracene
Phenanthrene	Pyrene-d <sub>10</sub> (DMC)	Benzo(g,h,i)perylene
Anthracene		Benzo(a)pyrene-d <sub>12</sub> (DMC)
Di-n-butylphthalate		
Fluoranthene		
4,6-Dinitro-2-methylphenol-d <sub>2</sub> (DMC)		
Anthracene-d <sub>10</sub> (DMC)		

Table D-3

Characteristic Ions for Semivolatile Organic Compounds

Target Compounds	Primary Ion	Secondary Ion(s)
Benzaldehyde	77	105, 106
Phenol	94	65, 66
bis(2-Chloroethyl)ether	93	63, 95
2-Chlorophenol	128	64, 130
2-Methylphenol	108	107
2,2'-oxybis(1-Chloropropane)	45	77, 79
Acetophenone	105	77, 51
4-Methylphenol	108	107
N-nitroso-di-n-propylamine	70	42, 101, 130
Hexachloroethane	117	201, 199
Nitrobenzene	77	123, 65
Isophorone	82	95, 138
2-Nitrophenol	139	65, 109
2,4-Dimethylphenol	107	121, 122
bis(-2-Chloroethoxy)methane	93	95, 123
2,4-Dichlorophenol	162	164, 98
Naphthalene	128	129, 127
4-Chloroaniline	127	129
Hexachlorobutadiene	225	223, 227
Caprolactam	113	55, 56
4-Chloro-3-methylphenol	107	144, 142
2-Methylnaphthalene	142	141
Hexachlorocyclopentadiene	237	235, 272
2,4,6-Trichlorophenol	196	198, 200
2,4,5-Trichlorophenol	196	198, 200
1,1'-Biphenyl	154	153, 76
2-Chloronaphthalene	162	164, 127
2-Nitroaniline	65	92, 138
Dimethyl phthalate	163	194, 164
Acenaphthylene	152	151, 153
3-Nitroaniline	138	108, 92
Acenaphthene	153	152, 154
2,4-Dinitrophenol	184	63, 154
4-Nitrophenol	109	139, 65
Dibenzofuran	168	139
2,4-Dinitrotoluene	165	63, 182
2,6-Dinitrotoluene	165	89, 121
Diethylphthalate	149	177, 150
1,2,4,5-Tetrachlorobenzene	216	214, 179, 108, 143, 218
4-Chlorophenyl-phenylether	204	206, 141
Fluorene	166	165, 167

Table D-3 (Con't)

Characteristic Ions for Semivolatile Organic Compounds

Target Compounds	Primary Ion	Secondary Ion(s)
4-Nitroaniline	138	92, 108
4,6-Dinitro-2-methylphenol	198	182, 77
N-Nitrosodiphenylamine	169	168, 167
4-Bromophenyl-phenylether	248	250, 141
Hexachlorobenzene	284	142, 249
Atrazine	200	173, 215
Pentachlorophenol	266	264, 268
Phenanthrene	178	179, 176
Anthracene	178	179, 176
Di-n-butylphthalate	149	150, 104
Fluoranthene	202	101, 100
Pyrene	202	101, 100
Butylbenzylphthalate	149	91, 206
3,3'-Dichlorobenzidine	252	254, 126
Benzo(a)anthracene	228	229, 226
bis(2-Ethylhexyl)phthalate	149	167, 279
Chrysene	228	226, 229
Di-n-octyl phthalate	149	-
Benzo(b)fluoranthene	252	253, 125
Benzo(k)fluoranthene	252	253, 125
Benzo(a)pyrene	252	253, 125
Indeno(1,2,3-cd)pyrene	276	138, 227
Dibenz(a,h)anthracene	278	139, 279
Benzo(g,h,i)perylene	276	138, 277
<b>Deuterated Monitoring Compounds</b>		
Phenol-d <sub>5</sub>	99	71, 42
bis-(2-Chloroethyl)ether-d <sub>8</sub>	67	99, 69
2-Chlorophenol-d <sub>4</sub>	132	134, 68, 66
4-Methylphenol-d <sub>8</sub>	113	115, 54
Nitrobenzene-d <sub>5</sub>	128	82, 54
2-Nitrophenol-d <sub>4</sub>	143	69, 41, 42
2,4-Dichlorophenol-d <sub>3</sub>	165	167, 101
4-Chloroaniline-d <sub>4</sub>	131	133, 69
Dimethylphthalate-d <sub>6</sub>	166	78
Acenaphthylene-d <sub>8</sub>	160	80, 158
4-Nitrophenol-d <sub>4</sub>	143	113, 41, 42
Fluorene-d <sub>10</sub>	176	174, 87, 86
4,6-Dinitro-2-methylphenol-d <sub>2</sub>	200	170, 52
Anthracene-d <sub>10</sub>	188	94, 80
Pyrene-d <sub>10</sub>	212	106, 104
Benzo(a)pyrene-d <sub>12</sub>	264	132, 118



Table D-3 (Con't)

Characteristic Ions for Semivolatile Organic Compounds

Internal Standard Compounds	Primary Ion	Secondary Ion(s)
1,4-Dichlorobenzene-d <sub>4</sub>	152	115
Naphthalene-d <sub>8</sub>	136	68
Acenaphthene-d <sub>10</sub>	164	162, 160
Phenanthrene-d <sub>10</sub>	188	94, 80
Chrysene-d <sub>12</sub>	240	120, 236
Perylene-d <sub>12</sub>	264	260, 265

Table D-4

Acceptance Criteria for Initial and Continuing Calibration of  
Semivolatile Target Compounds and Deuterated Monitoring Compounds

Semivolatile Compounds	Minimum RRF	Maximum %RSD	Maximum %Diff
Benzaldehyde	0.010	none	none
Phenol	0.800	20.5	±25.0
bis-(2-Chloroethyl)ether	0.700	20.5	±25.0
2-Chlorophenol	0.800	20.5	±25.0
2-Methylphenol	0.700	20.5	±25.0
2,2'-oxybis-(1-Chloropropane)	0.010	none	none
Acetophenone	0.010	none	none
4-Methylphenol	0.600	20.5	±25.0
N-Nitroso-di-n-propylamine	0.500	20.5	±25.0
Hexachloroethane	0.300	20.5	±25.0
Nitrobenzene	0.200	20.5	±25.0
Isophorone	0.400	20.5	±25.0
2-Nitrophenol	0.100	30.0	±30.0
2,4-Dimethylphenol	0.200	30.0	±30.0
bis-(2-Chloroethoxy)methane	0.300	20.5	±25.0
2,4-Dichlorophenol	0.200	20.5	±25.0
Naphthalene	0.700	20.5	±25.0
4-Chloroaniline	0.010	none	none
Hexachlorobutadiene	0.010	none	none
Caprolactam	0.010	none	none
4-Chloro-3-Methylphenol	0.200	20.5	±25.0
2-Methylnaphthalene	0.400	20.5	±25.0
Hexachlorocyclopentadiene	0.010	none	none
2,4,6-Trichlorophenol	0.200	20.5	±25.0
2,4,5-Trichlorophenol	0.200	20.5	±25.0
1,1'-Biphenyl	0.010	none	none
2-Chloronaphthalene	0.800	20.5	±25.0
2-Nitroaniline	0.010	none	none
Dimethylphthalate	0.010	none	none
2,6-Dinitrotoluene	0.200	20.5	±25.0
Acenaphthylene	0.900	20.5	±25.0
3-Nitroaniline	0.010	none	none
Acenaphthene	0.900	20.5	±25.0
2,4-Dinitrophenol	0.010	none	none
4-Nitrophenol	0.010	none	none
Dibenzofuran	0.800	20.5	±25.0
2,4-Dinitrotoluene	0.200	30.0	±30.0
Diethylphthalate	0.010	none	none
1,2,4,5-Tetrachlorobenzene	0.010	none	none
4-Chlorophenyl-phenylether	0.400	20.5	±25.0
Fluorene	0.900	20.5	±25.0
4-Nitroaniline	0.010	none	none
4,6-Dinitro-2-Methylphenol	0.010	none	none
4-Bromophenyl-phenylether	0.100	20.5	±25.0
N-Nitrosodiphenylamine	0.010	none	none
Hexachlorobenzene	0.100	20.5	±25.0
Atrazine	0.010	none	none
Pentachlorophenol	0.050	20.5	±25.0
Phenanthrene	0.700	20.5	±25.0

Table D-4 (Con't)

Acceptance Criteria for Initial and Continuing Calibration of  
Semivolatile Target Compounds and Deuterated Monitoring Compounds

Semivolatile Compounds	Minimum RRF	Maximum %RSD	Maximum %Diff
Anthracene	0.700	20.5	±25.0
Di-n-butylphthalate	0.010	none	none
Fluoranthene	0.600	20.5	±25.0
Pyrene	0.600	20.5	±25.0
Butylbenzylphthalate	0.010	none	none
3,3'-Dichlorobenzidine	0.010	none	none
Benzo(a)anthracene	0.800	20.5	±25.0
Chrysene	0.700	20.5	±25.0
bis-(2-Ethylhexyl)phthalate	0.010	none	none
Di-n-Octylphthalate	0.010	none	none
Benzo(b)fluoranthene	0.700	20.5	±25.0
Benzo(k)fluoranthene	0.700	20.5	±25.0
Benzo(a)pyrene	0.700	20.5	±25.0
Indeno(1,2,3-cd)pyrene	0.500	20.5	±25.0
Dibenzo(a,h)anthracene	0.400	20.5	±25.0
Benzo(g,h,i)perylene	0.500	20.5	±25.0
Deuterated Monitoring Compounds			
Phenol-d <sub>5</sub>	0.010	none	none
bis-(2-Chloroethyl)ether-d <sub>8</sub>	0.010	none	none
2-Chlorophenol-d <sub>4</sub>	0.010	none	none
4-Methylphenol-d <sub>8</sub>	0.010	none	none
Nitrobenzene-d <sub>5</sub>	0.010	none	none
2-Nitrophenol-d <sub>4</sub>	0.010	none	none
2,4-Dichlorophenol-d <sub>3</sub>	0.010	none	none
4-Chloroaniline-d <sub>4</sub>	0.010	none	none
Dimethylphthalate-d <sub>6</sub>	0.010	none	none
Acenaphthylene-d <sub>8</sub>	0.010	none	none
4-Nitrophenol-d <sub>4</sub>	0.010	none	none
Fluorene-d <sub>10</sub>	0.010	none	none
4,6-Dinitro-2-methylphenol-d <sub>2</sub>	0.010	none	none
Anthracene-d <sub>10</sub>	0.010	none	none
Pyrene-d <sub>10</sub>	0.010	none	none
Benzo(a)pyrene-d <sub>12</sub>	0.010	none	none

Table D-5

Deuterated Monitoring Compound Recovery Limits

Compound	% Recovery
Phenol-d <sub>5</sub>	10-110
bis-(2-Chloroethyl)ether-d <sub>8</sub>	41-94
2-Chlorophenol-d <sub>4</sub>	33-110
4-Methylphenol-d <sub>8</sub>	38-95
Nitrobenzene-d <sub>5</sub>	35-114
2-Nitrophenol-d <sub>4</sub>	40-106
2,4-Dichlorophenol-d <sub>3</sub>	42-98
4-Chloroaniline-d <sub>4</sub>	8-70
Dimethylphthalate-d <sub>6</sub>	62-102
Acenaphthylene-d <sub>8</sub>	49-98
4-Nitrophenol-d <sub>4</sub>	9-181
Fluorene-d <sub>10</sub>	50-97
4,6-Dinitro-2-methylphenol-d <sub>2</sub>	53-153
Anthracene-d <sub>10</sub>	55-116
Pyrene-d <sub>10</sub>	47-114
Benzo(a)pyrene-d <sub>12</sub>	54-120

Table D-6

Matrix Spike Recovery and Relative Percent Difference Limits

Compound	% Recovery	RPD
Phenol	12-110	42
2-Chlorophenol	27-123	40
N-Nitroso-di-n-propylamine	41-116	38
4-Chloro-3-methylphenol	23-97	42
Acenaphthene	46-118	31
4-Nitrophenol	10-80	50
2,4-Dinitrotoluene	24-96	38
Pentachlorophenol	9-103	50
Pyrene	26-127	31

EXHIBIT D

METHOD FOR THE ANALYSIS OF LOW CONCENTRATION WATER FOR  
PESTICIDES AND AROCLORS

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# Exhibit D -- Analytical Methods for Pesticides/Aroclors

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1.0 SCOPE AND APPLICATION

- 1.1 The analytical method that follows is designed to analyze water in order to determine the presence and concentrations of the chlorinated pesticides and Aroclors found in the Target Compound List (Exhibit C - Pesticides). The majority of the samples are expected to be from drinking water and well/ground water type sources around Superfund sites. The method can be used for determining analyte concentrations as low as ten parts per trillion. The method is based on EPA Method 608. The method includes sample extraction, extract cleanup techniques, and the Gas Chromatograph/Electron Capture Detector (GC/ECD) analytical method for chlorinated pesticides and aroclors.
- 1.2 Resolution difficulties have been associated with the following pairs of compounds using this method:
- On a DB-608 or equivalent column, DDE and Dieldrin; Methoxychlor and Endrin ketone; and Endosulfan I and gamma-Chlordane.
  - On a DB-1701 or equivalent column, Endosulfan I and gamma-Chlordane; and Methoxychlor and Endosulfan sulfate.
- 1.3 There are two isomers of heptachlor epoxide, the endo epoxy isomer (isomer A) and the exo epoxy isomer (isomer B). The two isomers are separable using current GC capillary columns. Only the exo epoxy isomer (isomer B) is of environmental significance. This is the isomer that must be used as an analytical standard, identified and quantitated in sample analysis, and reported on appropriate forms as heptachlor epoxide.

Exhibit D Pesticides/Aroclors -- Sections 2 & 3  
Summary of Method

2.0 SUMMARY OF METHOD

- 2.1 A one liter aliquot of sample is spiked with the surrogate solution and extracted with methylene chloride by using a continuous liquid-liquid extractor or separatory funnel. The methylene chloride extract is dried and concentrated, exchanged to hexane, cleaned up to remove interferences, and adjusted to a final volume of 2.0 milliliters (mL).
- 2.2 The hexane extract is injected onto two wide-bore capillary columns in a Gas Chromatograph (GC). The GC is temperature programmed to separate the pesticides and Aroclors which are then detected with an Electron Capture Detector (ECD). Calibration and run sequence specifications of the GC/ECD method apply independently to each GC column.
- 2.3 A single component pesticide is identified if a peak is detected within its appropriate Retention Time (RT) window on each of two GC columns. Quantitative analysis of pesticides/Aroclors must be accomplished by the external standard method. Single component analytes and the surrogates must be analyzed at three concentration levels during the initial calibration.
- 2.4 Toxaphene and Aroclors are identified primarily by pattern recognition, but RTs of three to five major peaks must also be taken into consideration. Single-point calibrations for multicomponent analytes are sufficient for quantitation by this method. Standards for identified Aroclors and Toxaphene must be run within 72 hours of the sample analysis in which they were observed. These standards are used to verify identification only; quantitation is based on the standards analyzed during initial calibration.

3.0 DEFINITIONS

See Exhibit G for a complete list of definitions.

#### 4.0 INTERFERENCES

##### 4.1 Method Interferences

Method interferences may be caused by contaminants in solvents, reagents, glassware, and sample processing hardware. These contaminants lead to discrete artifacts or to elevated baselines in gas chromatograms. These materials must be routinely demonstrated to be free from interferences under the sample preparation and analysis conditions by analyzing instrument blanks and method blanks. Interferences caused by phthalate esters can pose a major problem in pesticide analysis. Because common flexible plastics contain varying amounts of phthalates which are easily extracted during laboratory operations, cross-contamination of glassware frequently occurs when plastics are handled. Interferences from phthalates can best be minimized by avoiding the use of such plastics in the laboratory.

##### 4.2 Matrix Interferences

Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature of the site being sampled. The cleanup procedures in this method must be used to remove such interferences in order to achieve the Contract Required Quantitation Limits (CRQL).

#### 5.0 SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these reagents should be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets should be made available to all personnel involved in these analyses. Specifically, concentrated sulfuric acid and the 10 N sodium hydroxide solution are moderately toxic and extremely irritating to skin and mucous membranes. Use these reagents in a fume hood whenever possible and if eye or skin contact occurs, flush with large volumes of water. Always wear safety glasses or a shield for eye protection, protective clothing, and observe proper mixing when working with these reagents.

5.2 The following analytes covered by this method have been tentatively classified as known or suspected human or mammalian carcinogens: 4,4'-DDT, 4,4'-DDD, the BHCs, and the Aroclors. Primary standards of these toxic compounds should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

Exhibit D Pesticides/Aroclors -- Section 6  
Equipment and Supplies

6.0 EQUIPMENT AND SUPPLIES

Brand names, suppliers, and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and supplies other than those specified here, but demonstration of equivalent performance meeting the requirements of the Statement of Work (SOW) is the responsibility of the Contractor. The Contractor must document in its Sample Delivery Group (SDG) Narrative when it uses equipment and supplies other than those specified here.

6.1 Glassware

6.1.1 Continuous Liquid-Liquid Extractors

Continuous Liquid-Liquid Extractors equipped with PTFE or glass connecting joints and stopcocks requiring no lubrication (Hershberg-Wolf extractor, Ace Glass Company, Vineland, NJ P/N 6841-10 or equivalent) or Hydrophobic Membrane-based Extractor (Accelerated One Step™ Extractor, Corning series 3195 or equivalent).

6.1.2 Separatory Funnels - 2 liter with PTFE stopcock.

6.1.3 Graduated Cylinder - 1 liter capacity.

6.1.4 Drying column, chromatographic column approximately 400 millimeters (mm) long x 19 mm ID, with coarse frit. (Substitution of a small pad of disposable Pyrex glass wool for the frit will help prevent cross-contamination of sample extracts.)

6.1.5 Kuderna-Danish Apparatus

6.1.5.1 Concentrator Tubes - 10 milliliters (mL), graduated (Kontes, K-570050-1025, or equivalent).

6.1.5.2 Evaporative Flasks - 500 mL (Kontes K-570001-0500, or equivalent). Attach to concentrator tube with springs.

6.1.5.3 Snyder Columns - three-ball macro (Kontes K-50300-0121, or equivalent).

6.1.5.4 Snyder Columns, micro two or three ball with a 19 mm ground glass joint.

6.1.6 Pipet, Volumetric 1.00 mL or 2.00 mL.

6.1.7 Microsyringe, 1.0 microliter (μL) and larger, 0.006 (0.15 mm) inch ID needle.

6.1.8 Syringe, 1.00 mL or 2.00 mL (optional).

6.1.9 Volumetric flask, 10.00 mL, and 1 or 2 mL.

6.1.10 Vials and caps, 20 and 10 mL, with screw cap and PTFE or aluminum foil liner, 2 or 1 mL for Gas Chromatograph (GC) auto sampler.

6.1.11 Bottle or test tube, 20 mL with PTFE-lined screw cap for sulfur removal.

6.1.12 Centrifuge tubes, calibrated, 12 mL, for sulfur removal.

6.1.13 Micropipet, 200 μL, with disposable tips.

6.2 Florisil Cleanup Equipment

- 6.2.1 Florisil bonded silica. 1 g cartridges with stainless steel or PTFE frits, Catalog No. 694-313 (Analytichem, 24201 Frampton Ave., Harbor City, CA, or equivalent).
- 6.2.2 Vacuum system for eluting multiple cleanup cartridges. Vac Elute Manifold, Analytichem International, J.T. Baker, or Supelco (or equivalent).
- 6.2.3 Vacuum trap made from a 500 mL sidearm flask fitted with a one-hole stopper and glass tubing.
- 6.2.4 Vacuum pressure gauge.
- 6.2.5 Rack for holding 10 mL volumetric flasks in the manifold.

NOTE: Other types of equivalent systems, such as an automated system using syringe pressure are considered acceptable for elution of Florisil cartridges, as long as all quality control (QC) and sample technical acceptance criteria are met.

6.3 pH Paper, Wide Range

- 6.4 pH Meter -- With a combination glass electrode. Calibrate according to manufacturer's instructions. pH meter must be calibrated prior to each use.

6.5 Boiling Chips

- 6.5.1 Silicon carbide boiling chips, approximately 10 to 40 mesh. Heat the chips to 400°C for 30 minutes or solvent rinse before use.
- 6.5.2 PTFE boiling chips (optional). Solvent rinse the chips before use.

- 6.6 Water Bath, heated, with concentric ring cover, capable of temperature control.

NOTE: To prevent the release of solvent fumes into the laboratory, the water bath must be used in a hood.

6.7 Balances

Analytical balances, capable of weighing accurately to  $\pm 0.0001$  g. The balances must be calibrated with class S weights or known reference weights once per each 12-hour work shift. The balances must be calibrated with class S weights at a minimum of once per month. The balances must also be annually checked by a certified technician.

6.8 Nitrogen Evaporation Device

Nitrogen evaporation device equipped with a heated bath that can be maintained at 35 to 40°C (N-Evap by Organomation Associates, Inc., South Berlin, MA, or equivalent). To prevent the release of solvent fumes into the laboratory, the nitrogen evaporation device must be used in a hood.

6.9 Mechanical Shaker or Mixer, for Sulfur Removal

Exhibit D Pesticides/Aroclors -- Section 6  
Equipment and Supplies (Con't)

6.10 Gas Chromatograph/Electron Capture Detector (GC/ECD) System

6.10.1 Gas Chromatograph (GC)

6.10.1.1 The GC must adequately regulate temperature in order to give a reproducible temperature program and have a flow controller that maintains a constant column flow rate throughout temperature program operations. The system must have all required accessories including syringes, analytical columns, and gases.

6.10.1.2 GCs that are available from some manufacturers may have difficulty in meeting certain method QC requirements because of endrin and DDT breakdown in the injector. This problem can be minimized by operating the injector at 200-205°C, using a Pyrex (not quartz) methyl silicone deactivated injector liner, and deactivating the metal parts in the injector with dichlorodimethyl silane. In some cases, using a 0.25 inch packed column injector converted for use with 0.53 mm capillary columns works better than a Grob-type injector. If a Grob-type injector is used, a 4 mm liner may be required to meet breakdown criteria.

6.10.1.3 Gas Chromatograph Columns -- Two wide-bore (0.53 mm ID) fused silica GC columns are required. A separate detector is required for each column. The specified analytical columns are a 30 m x 0.53 mm ID, 1.0 µm film thickness DB-1701 (J&W Scientific); SPB 1701 (Supelco); AT 1701 (Alltech); RTX-1701 (Restek); CP-Sil 19CB (Chrompack); 007-1701 (Quadrex); BP-10 (SGE); or equivalent, and a 30 m x 0.53 mm ID, 0.5 to 1.0 micrometer (µm) film thickness DB-608 (J&W Scientific); HP-608 (Hewlett Packard); SPB-608 (Supelco); 007-608 (Quadrex); BP-608 (SGE); CP-Sil 8CB (Chrompack); or equivalent.

NOTE: The column length stated above is the minimum requirement. Longer columns that meet resolution and calibration requirements may be used. A description of the GC columns used for analysis shall be provided in the SDG Narrative.

6.10.1.3.1 A capillary column is considered equivalent if:

- The column does not introduce contaminants which interfere with identification and quantitation of the compounds listed in Exhibit C (Pesticides).
- The analytical results generated using the column meet the initial calibration and calibration verification technical acceptance criteria listed in the SOW and the Contract Required Quantitation Limits (CRQLs) listed in Exhibit C (Pesticides).
- The column can accept at least 16 times the low point standard for individual standard mixtures A and B for each compound listed in Exhibit C (Pesticides) without becoming overloaded.
- The column pair chosen must have dissimilar phases/chemical properties in order to separate the compounds of interest in different Retention Time (RT) order.

6.10.1.3.2 Although the instructions included in the SOW are for wide bore capillary columns, narrower bore capillary columns may be evaluated for use. Follow manufacturer's instructions for use

of its product. Document in SDG Narrative if other columns are used by specifying the column used (Exhibit B Section 2.5.1).

- 6.10.1.3.3 As applicable, follow the manufacturer's instructions for use of its product.
- 6.10.1.3.4 The Contractor must maintain documentation that the alternate column met the criteria in Sections 9.2.5 and 9.3.5. The minimum documentation is as follows:
- 6.10.1.3.4.1 Manufacturer provided information concerning the performance characteristics of the column;
- 6.10.1.3.4.2 GC chromatograms and data system reports generated on the GC/ECD and used for CLP analyses:
- From instrument blanks which demonstrate that there are no contaminants which interfere with the pesticide analysis when using the alternate column;
  - For initial calibration standards analyzed using the alternate column; and
  - For calibration verification standards analyzed using the alternate column.
- 6.10.1.3.5 Based on the Contractor generated data described in Section 6.10.1.3.4.2, the Contractor must complete a written comparison and review, signed by the Laboratory Manager certifying that:
- The alternate column performance is comparable to the required column performance in its ability to produce initial calibrations and calibration verifications which meet the technical acceptance criteria in Sections 9.2.5 and 9.3.5;
  - The low point initial calibration standard analyses have adequate sensitivity to meet the pesticide CRQLs;
  - The high point initial calibration standard analyses were not overloaded; and
  - The alternate column does not introduce contaminants which interfere with identification and quantitation of compounds listed in Exhibit C (Pesticides).
- 6.10.1.3.6 The documentation must be made available to USEPA during on-site laboratory evaluations or sent to USEPA upon request of the Contract Laboratory Program Project Officer (CLP PO).
- 6.10.1.3.7 PACKED COLUMNS CANNOT BE USED.
- 6.10.1.4 Columns are mounted in a 0.25-inch injector ports by using glass adapters available from a variety of commercial sources (J&W Scientific, Supelco, Inc., Hewlett-Packard, Varian, Inc., Perkin Elmer, or equivalent). The two columns may be mounted into a single injection port with a tee adapter (Supelco, Inc., Bellefonte, PA, Catalog No. 2-3660, or equivalent). Use of this adapter allows simultaneous injection onto both columns. The laboratory should follow manufacturer's recommendations for mounting 0.53 mm capillary columns in injector ports.



Exhibit D Pesticides/Aroclors -- Section 6  
Equipment and Supplies (Con't)

6.10.1.5 The carrier gas for routine applications is helium. Laboratories may choose to use hydrogen as a carrier gas, but they must clearly identify its use in the SDG Narrative and on all divider pages preceding raw chromatographic data in submissions to USEPA. Laboratories that choose to use hydrogen are advised to exercise caution in its use. Use of a hydrogen leak detector is highly recommended when hydrogen is used as the carrier gas. All GC carrier gas lines must be constructed from stainless steel or copper tubing. Non-polytetrafluoroethylene (PTFE) thread sealants or flow controllers with rubber components are not to be used.

6.10.2 Electron Capture Detector (ECD)

The linearity of the response of the ECD may be greatly dependent on the flow rate of the make-up gas. The make-up gas must be P-5, P-10 (argon/methane) or nitrogen according to the instrument specification. Care must be taken to maintain stable and appropriate flow of make-up gas to the detector. The GC/ECD system must be in a room in which the atmosphere has been demonstrated to be free of all contaminants which may interfere with the analysis. The instrument must be vented to outside the facility or to a trapping system which prevents the release of contaminants into the instrument room.

6.10.3 Data System

A data system must be interfaced to the GC/ECD. The data system must allow the continuous acquisition of data throughout the duration of the chromatographic program and must permit, at the minimum, the output of time vs. intensity (peak height or peak area) data. Also, the data system must be able to rescale chromatographic data in order to report chromatograms meeting the requirements listed within this method.

6.10.4 Magnetic Tape Storage Device

Magnetic tape storage devices must be capable of recording data and suitable for long-term, off-line storage of GC/ECD data.

7.0 REAGENTS AND STANDARDS

7.1 Reagents

Reagents shall be dated with the receipt date and used on a first-in, first-out basis. The purity of the reagents shall be verified before use.

- 7.1.1 Reagent water -- Defined as water in which no target analyte is observed at the Contract Required Quantitation Limits (CRQL) for that compound.
- 7.1.1.1 Reagent water may be generated by passing tap water through a carbon filter bed containing about 453 grams (g) (1 pound) of activated carbon (Calgon Corp., Filtrasorb-300, or equivalent).
- 7.1.1.2 Reagent water may be generated using a water purification system (Millipore Super-Q or equivalent).
- 7.1.2 Sodium sulfate, granular-anhydrous reagent grade, heated at 400°C for 4 hours, or at 120°C for 16 hours, cooled in a desiccator, and stored in a glass bottle. Each lot must be extracted with hexane and analyzed by Gas Chromatograph/Electron Capture Detector (GC/ECD) to demonstrate that it is free of interference before use. J. T. Baker anhydrous granular, Catalog No. 3375, or equivalent.
- CAUTION:** An open container of sodium sulfate may become contaminated during storage in the laboratory.
- 7.1.3 Methylene chloride, hexane, acetone, toluene, iso-octane, and methanol (optional), pesticide quality, or equivalent. It is recommended that each lot of solvent be analyzed to demonstrate that it is free of interference before use. Methylene chloride must be certified as acid free or must be tested to demonstrate that it is free of hydrochloric acid. Acidic methylene chloride must be passed through basic alumina and then demonstrated to be free of hydrochloric acid.
- 7.1.4 Mercury, triple distilled, for sulfur clean-up.
- 7.1.5 Copper powder (optional), fine, granular (Mallinckrodt 4649 or equivalent). Copper may be used instead of mercury for sulfur clean-up. Remove oxides by treating with dilute nitric acid, rinse with distilled water to remove all traces of acid, rinse with acetone, and dry under a stream of nitrogen.
- 7.1.6 Sodium hydroxide solution (10 N). Carefully dissolve 40 g of NaOH in reagent water and dilute the solution to 100 milliliters (mL).
- 7.1.7 Concentrated sulfuric acid, (Sp. Gr. 1.84)-36N.
- 7.1.8 Nitric acid, dilute, for sulfur removal with copper.
- 7.1.9 Ten percent acetone in hexane (v/v). Prepare by adding 10.0 mL of acetone to 90.0 mL of hexane.

NOTE: Prepare this mixture accurately or the results from the Florisil cartridge cleanup will be adversely affected. Water in the acetone will also adversely affect Florisil performance.

Exhibit D Pesticides/Aroclors -- Section 7  
Reagents and Standards (Con't)

7.2 Standards

The Contractor must provide all standards to be used with this contract. These standards may be used only after they have been certified according to the procedure in Exhibit E. The Contractor must be able to verify that the standards are certified. Manufacturer's certificates of analysis must be retained by the Contractor and presented upon request.

7.2.1 Stock Standard Solutions

- 7.2.1.1 Stock standard solutions may be purchased as certified solutions or prepared from pure standard materials.
- 7.2.1.2 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in toluene, dilute to volume in a 10 mL volumetric flask with toluene or acetone. Larger volumes may be used at the convenience of the analyst.
- 7.2.1.3 When compound purity is assayed to be 97 percent or greater, the weight may be used without correction to calculate the concentration of the stock solution. If the compound purity is assayed to be less than 97 percent, the weight must be corrected when calculating the concentration of the stock solution.
- 7.2.1.4 Fresh stock standards must be prepared once every six months, or sooner, if standards have degraded or concentrated. Stock standards must be checked for signs of degradation or concentration just prior to preparing working standards from them.

7.2.2 Secondary Dilution Standards

- 7.2.2.1 Using stock standards, prepare secondary dilution standards in acetone that contain the compounds of interest either singly or mixed together.
- 7.2.2.2 Fresh secondary dilution standards must be prepared once every six months, or sooner, if standards have degraded or concentrated. Secondary dilution standards must be checked for signs of degradation or concentration just prior to preparing working standards from them.

7.2.3 Working Standards

7.2.3.1 Surrogate Standard Spiking Solution

The surrogates, tetrachloro-m-xylene and decachlorobiphenyl, are added to all standards, samples (including Laboratory Control Samples), matrix spike, matrix spike duplicates and if required, Performance Evaluation (PE) samples, and required blanks (method/sulfur clean-up/instrument). Prepare a surrogate spiking solution of 0.20 micrograms per milliliter ( $\mu\text{g/mL}$ ) of each of the two compounds in acetone. The solution should be checked frequently for stability. The solution must be replaced every 6 months, or sooner if the solution has degraded or concentrated.

7.2.3.2 Matrix Spiking Solution

Prepare a matrix spiking solution in acetone or methanol that contains the following pesticides at the concentrations specified. The solution must be replaced every six months, or sooner if the solution has degraded or concentrated.

Exhibit D Pesticides/Aroclors -- Section 7  
Reagents and Standards (Con't)

<u>Pesticide</u>	<u>Concentration (µg/mL)</u>
gamma- BHC (Lindane)	0.1
4,4'-DDT	0.2
Endrin	0.2
Heptachlor	0.1
Aldrin	0.1
Dieldrin	0.2

7.2.3.3 Resolution Check Mixture

The Resolution Check Mixture is composed of the pesticides and surrogates at the concentrations listed below in hexane or iso-octane. The mixture must be prepared every six months, or sooner, if the solution has degraded or concentrated.

<u>Compounds</u>	<u>Concentration (ng/mL)</u>
gamma- Chlordane	10.0
Endosulfan I	10.0
4,4'-DDE	20.0
Dieldrin	20.0
Endosulfan sulfate	20.0
Endrin ketone	20.0
Methoxychlor	100.0
Tetrachloro-m-xylene	20.0
Decachlorobiphenyl	20.0

7.2.3.4 Performance Evaluation Mixture (PEM)

The PEM is prepared in hexane or iso-octane, as listed below. The PEM must be prepared weekly, or sooner if the solution has degraded or concentrated.

<u>Compounds</u>	<u>Concentration (ng/mL)</u>
gamma-BHC	10.0
alpha-BHC	10.0
4,4'-DDT	100.0
beta-BHC	10.0
Endrin	50.0
Methoxychlor	250.0
Tetrachloro-m-xylene	20.0
Decachlorobiphenyl	20.0

Exhibit D Pesticides/Aroclors -- Section 7  
Reagents and Standards (Con't)

7.2.3.5 Individual Standard Mixtures A and B

The Individual Standard Mixture solutions must be prepared in either hexane or iso-octane. The concentrations of the pesticides in the low point standard mixtures are given below. The midpoint concentration must be 4 times the low point concentration for each analyte, including the surrogates. The high concentration must be at least 16 times the low point concentration for each analyte, including the surrogates, but a higher concentration may be chosen by the Contractor. The high point concentration defines the upper end of the concentration range for which the calibration is valid. The solution must be prepared every six months, or sooner, if the solution has degraded or concentrated.

Individual Standard Mix A	Low Point Concentration (ng/mL)	Individual Standard Mix B	Low Point Concentration (ng/mL)
alpha-BHC	5.0	beta-BHC	5.0
Heptachlor	5.0	delta-BHC	5.0
gamma-BHC	5.0	Aldrin	5.0
Endosulfan I	5.0	Heptachlor-epoxide (exo-epoxy isomer)	5.0
Dieldrin	10.0	alpha-Chlordane	5.0
Endrin	10.0	gamma-Chlordane	5.0
4,4'-DDD	10.0	4,4'-DDE	10.0
4,4'-DDT	10.0	Endosulfan sulfate	10.0
Methoxychlor	50.0	Endrin aldehyde	10.0
Tetrachloro-m-xylene	5.0	Endrin ketone	10.0
Decachlorobiphenyl	10.0	Endosulfan II	10.0
		Tetrachloro-m-xylene	5.0
		Decachloro-biphenyl	10.0

NOTE: Only the exo-epoxy isomer (isomer B) of heptachlor epoxide is used as an analytical standard.

7.2.3.6 Multicomponent Standards

Toxaphene and Aroclor standards must be prepared individually except for Aroclor 1260 and Aroclor 1016 which may be combined in one standard mixture. The calibration standards for the Aroclors must be prepared at concentrations of 100 nanograms (ng)/mL, except for Aroclor 1221 which must be prepared at 200 ng/mL. Toxaphene must be prepared at 500 ng/mL. All multicomponent standards must contain the surrogates at 20.0 ng/mL. The Aroclor and toxaphene solutions must be prepared in hexane or iso-octane. Each solution must be prepared every 6 months, or sooner, if the solution has degraded or concentrated.

7.2.3.7 Florisil Cartridge Check Solution

Prepare a 0.10 µg/mL solution of 2,4,5-trichlorophenol in acetone. The solution must be prepared every six months, or sooner, if the solution has degraded or concentrated.

7.2.3.8 Laboratory Control Sample (LCS) Spiking Solution

Prepare a LCS spiking solution that contains each of the analytes at the concentrations listed below in methanol or acetone. The LCS solution must be prepared every six months, or sooner, if the solution has degraded or concentrated.

<u>Compounds</u>	<u>Concentration (µg/mL)</u>
gamma-BHC	0.10
Heptachlor epoxide	0.10
Dieldrin	0.20
4,4'-DDE	0.20
Endrin	0.20
Endosulfan sulfate	0.20
gamma-Chlordane	0.10

7.2.4 Ampulated Standard Extracts

Standard solutions purchased from a chemical supply house as ampulated extracts in glass vials may be retained and used until the expiration date provided by the manufacturer. If no manufacturer's expiration date is provided, the standard solutions as ampulated extracts may be retained and used for 2 years from the preparation date. Standard solutions prepared by the Contractor which are immediately ampulated in glass vials may be retained for 2 years from preparation date. Upon breaking the glass seal, the expiration times listed in Sections 7.2.1 to 7.2.3 will apply. The Contractor is responsible for assuring that the integrity of the standards has not degraded (Section 7.2.5.5).

7.2.5 Storage of Standards

- 7.2.5.1 Store the stock and secondary standard solutions at 4°C (±2°C) in PTFE-lined, screw-cap, amber bottles/vials.
- 7.2.5.2 Store the working standard solutions at 4°C (±2°C) in PTFE-lined screw-cap, amber bottles/vials. The working standards must be checked frequently for signs of degradation or evaporation.
- 7.2.5.3 Protect all standards from light.
- 7.2.5.4 Samples, sample extracts, and standards must be stored separately.
- 7.2.5.5 The Contractor is responsible for maintaining the integrity of standard solutions and verifying prior to use. Storage of standard solutions in the freezer may cause some compounds to precipitate. This means at the minimum, the standards must be brought to room temperature prior to use, checked for losses, and checked that all components have remained in solution. Additional steps may be necessary to ensure all components are in solution.

7.2.6 Temperature Records for Storage of Standards

- 7.2.6.1 The temperature of all standard storage refrigerators/freezers shall be recorded daily.
- 7.2.6.2 Temperature excursions shall be noted and appropriate corrective actions shall be taken to correct problems, when required.

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7.2.6.3 Corrective action SOPs shall be posted on the refrigerators.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Sample Collection and Preservation

8.1.1 Water samples may be collected in 1 L (or 1 quart) amber glass containers, fitted with screw-caps lined with PTFE. If amber containers are not available, the samples should be protected from light. The specific requirements for site sample collection are outlined by the Region.

8.1.2 All samples must be iced or refrigerated at 4°C (±2°C) from the time of collection until extraction.

8.2 Procedure for Sample Storage

8.2.1 The samples must be protected from light and refrigerated at 4°C (±2°C) from the time of receipt until 60 days after delivery of a complete reconciled sample data package to USEPA. After 60 days the samples may be disposed of in a manner that complies with all applicable regulations.

8.2.2 The samples must be stored in an atmosphere demonstrated to be free of all potential contaminants.

8.3 Procedure for Sample Extract Storage

8.3.1 Sample extracts must be protected from light and stored at 4°C (±2°C) until 365 days after delivery of a complete reconciled data package to USEPA.

8.3.2 Sample extracts must be stored in an atmosphere demonstrated to be free of all potential contaminants.

8.3.3 Samples, sample extracts, and standards must be stored separately.

8.4 Records for Sample and Sample Extract Storage

8.4.1 The temperature of all sample and sample extract storage refrigerators shall be recorded daily.

8.4.2 Temperature excursions shall be noted and appropriate corrective actions shall be taken to correct problems, when required.

8.4.3 Corrective action SOPs shall be posted on the refrigerators.

8.5 Contract Required Holding Times

8.5.1 Extraction of water samples by separatory funnel procedures must be completed within 5 days of the Validated Time of Sample Receipt (VTSR). Extraction of water samples by continuous liquid-liquid extraction must be started within 5 days of VTSR.

8.5.2 As part of USEPA's QA program, USEPA may provide Performance Evaluation (PE) Samples as standard extracts which the Contractor is required to prepare per instructions provided by USEPA. PE samples must be prepared and analyzed concurrently with the samples in the SDG. The extraction holding time (5 days after VTSR) does not apply for PE Samples received as standard extracts.

8.5.3 Analysis of sample extracts must be completed within 40 days following the start of extraction.

## 9.0 CALIBRATION AND STANDARDIZATION

### 9.1 Gas Chromatograph (GC) Operating Conditions

9.1.1 The following are the gas chromatographic analytical conditions. The conditions are recommended unless otherwise noted.

Carrier Gas:	Helium (Hydrogen may be used, Section 6.10.1.5)
Column Flow:	5 mL/min
Make-up Gas:	Argon/Methane (P-5 or P-10) or N <sub>2</sub> (required)
Injector Temperature:	> 200°C (Section 9.1.5)
Injection Technique:	On-column
Injection Volume:	1 or 2 µL (Section 9.1.3)
Injector:	Grob-type, splitless
Initial Temperature:	150°C
Initial Hold Time:	0.5 min
Temperature Ramp:	5°C to 6°C/min
Final Temperature:	275°C
Final Hold Time:	After Decachlorobiphenyl has eluted (approximately 10 minutes)

9.1.2 Optimize GC conditions for analyte separation and sensitivity. Once optimized, the same GC conditions must be used for the analysis of all standards, samples (including Laboratory Control Samples, requested matrix spike, and matrix spike duplicate), and required blanks (method/sulfur clean-up/instrument).

9.1.3 Manual injections must be 2.0 microliter (µL). Auto injectors may use 1.0 µL volumes. The same injection volume must be used for all standards, samples (including Laboratory Control Samples, requested matrix spike, and matrix spike duplicate) and required blanks (method/sulfur clean-up/instrument).

9.1.4 The linearity of the Electron Capture Detector (ECD) may be greatly dependent on the flow rate of the make-up gas. Care must be taken to maintain stable and appropriate flow of make-up gas to the detector.

9.1.5 Cold (ambient temperature) on-column injectors that allow injection directly onto a 0.53 mm ID column may be used as long as the initial calibration and calibration verification technical acceptance criteria are met.

### 9.2 Initial Calibration

#### 9.2.1 Summary of Initial Calibration

Prior to sample (including Laboratory Control Samples, requested matrix spike and matrix spike duplicate) and required blanks



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(method/sulfur clean-up) analysis, each GC/ECD system must be initially calibrated at a minimum of three concentrations for single component analytes and surrogates in order to determine instrument sensitivity and the linearity of GC response. Multicomponent target analytes are calibrated at a single point.

9.2.2 Frequency of Initial Calibration

Each GC/ECD system must be initially calibrated upon award of the contract, whenever major instrument maintenance or modification is performed (e.g., column replacement or repair, cleaning or replacement of ECD, etc.), or if the calibration verification technical acceptance criteria have not been met.

9.2.3 Procedure for Initial Calibration

9.2.3.1 Set up the GC/ECD system as described in Section 9.1.

9.2.3.2 Prepare the initial calibration standards using the procedures, the analytes, and the concentrations according to Section 7.2.

9.2.3.3 All standards, samples (including Laboratory Control Samples, requested matrix spike, and matrix spike duplicate) and required blanks (method/sulfur clean-up) extracts must be allowed to warm to ambient temperature before analysis.

9.2.3.4 Analyze the initial calibration sequence as given below.

NOTE: Steps 16 and 17 are used as part of the calibration verification as well (Section 9.3).

INITIAL CALIBRATION SEQUENCE

1. Resolution Check
2. Performance Evaluation Mixture
3. Aroclor 1016/1260
4. Aroclor 1221
5. Aroclor 1232
6. Aroclor 1242
7. Aroclor 1248
8. Aroclor 1254
9. Toxaphene
10. Low Point Standard A
11. Low Point Standard B
12. Midpoint Standard A
13. Midpoint Standard B
14. High Point Standard A
15. High Point Standard B
16. Instrument Blank
17. Performance Evaluation Mixture

9.2.4 Calculations for Initial Calibration

9.2.4.1 During the initial calibration sequence, absolute Retention Times (RTs) are determined for all single component pesticides, the surrogates, and at least three major peaks of each multicomponent analyte.

- 9.2.4.2 For each single component pesticides, a RT is measured in each of the three calibration standards (low point, midpoint, high point) for Individual Standard Mixture A and Individual Standard Mixture B. **The RT for the surrogates is measured from each of the three analyses of Individual Standard Mixture A during the initial calibration.** The mean RT is calculated for each single component pesticide and surrogate as the average of the three values. Calculate a mean absolute RT for each single component pesticide and surrogate using Equation 1.

EQ. 1

$$\overline{RT} = \frac{\sum_{i=1}^n RT_i}{n}$$

Where:

$\overline{RT}$  = Mean absolute retention time of analyte.

$RT_i$  = Absolute retention time of analyte.

$n$  = Number of measurements (3).

- 9.2.4.3 A RT window is calculated for each single component analyte and surrogate and for the major peaks (3 to 5) of each multicomponent analyte by using Table D-1. Windows are centered around the average absolute RT for the analyte established during the initial calibration. Analytes are identified when peaks are observed in the RT window for the compound on both GC columns.
- 9.2.4.4 The linearity of the instrument is determined by calculating a percent relative standard deviation (%RSD) of the calibration factors from a three-point calibration curve for each of the single component pesticide and surrogates. Either peak area or peak height may be used to calculate calibration factors used in the %RSD equation. For example, it is permitted to calculate linearity for endrin based on peak area and to calculate linearity for aldrin based on peak height. It is not permitted within a %RSD calculation for an analyte to use calibration factors calculated from both peak area and peak height. For example, it is not permitted to calculate the calibration factor for the low point standard for endrin using peak height and calculate the midpoint and high point standard calibration factors for endrin using peak area.
- 9.2.4.5 Calculate the calibration factor for each single component pesticide and surrogate over the initial calibration range using Equation 2. The calibration factors for surrogates are calculated from the three analyses of Individual Standard A mixture only.
- 9.2.4.6 Calculate the mean and the %RSD of the calibration factors for each single component pesticide and surrogate over the initial calibration range using Equation 3 and Equation 4.

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EQ. 2

$$CF = \frac{\text{Peak area (or Height) of the standard}}{\text{Mass Injected (ng)}}$$

EQ. 3

$$\overline{CF} = \frac{\sum_{i=1}^n CF_i}{n}$$

EQ. 4

$$\%RSD = \frac{SD_{CF}}{\overline{CF}} \times 100$$

Where:

$$SD_{CF} = \sqrt{\frac{\sum_{i=1}^n (CF_i - \overline{CF})^2}{(n-1)}}$$

%RSD = Percent relative standard deviation.

SD<sub>CF</sub> = Standard deviation of calibration factors.

CF<sub>i</sub> = Calibration factor.

$\overline{CF}$  = Mean calibration factor.

n = Total number of values (3).

9.2.4.7 A calibration factor is calculated for each peak in a selected set of three to five major peaks for each multicomponent analyte using Equation 2.

9.2.4.8 Calculate the percent breakdown of DDT, the percent breakdown of Endrin, and the combined breakdown of DDT and Endrin in the Performance Evaluation Mixture (PEM) using Equations 5, 6, 7, and 8.

EQ. 5

$$\text{Amount found (ng)} = \frac{\text{Peak area (or Peak height) of compound in PEM}}{CF_{sp}}$$

Where:

$CF_{mp}$  = The calibration factor for the compound determined from the midpoint standard in the most recent initial calibration.

NOTE: If during the initial calibration, linearity was determined based on peak area for the compound, then the midpoint CF must be based on peak area. If during the initial calibration, the linearity for the compound was determined based on peak height for the compound, then the midpoint CF must be based on peak height.

EQ. 6

$$\% \text{Breakdown DDT} = \frac{\text{Amount found (ng) (DDD+DDE)}}{\text{Amount (ng) of DDT injected}} \times 100$$

EQ. 7

$$\% \text{Breakdown Endrin} = \frac{\text{Amount found (ng) (endrin aldehyde + endrin ketone)}}{\text{Amount (ng) of endrin injected}} \times 100$$

EQ. 8

$$\text{Combined \% Breakdown} = \% \text{Breakdown DDT} + \% \text{Breakdown Endrin}$$

9.2.4.9 Calculate the percent difference for each pesticide and surrogate in the PEM using Equations 5 and 9.

EQ. 9

$$\%D = \frac{C_{calc} - C_{nom}}{C_{nom}} \times 100$$

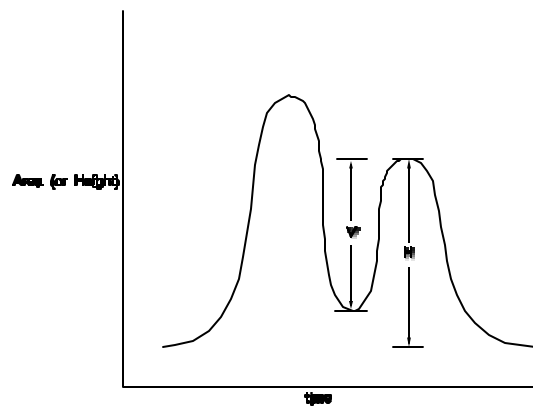
Where:

%D = Percent Difference.

$C_{nom}$  = Nominal concentration of each analyte.

$C_{calc}$  = Calculated concentration of each analyte from the analysis of the standard.

9.2.4.10 Calculate the resolution between the analytes in the Resolution Check Mixture, PEM and the midpoint concentrations of Individual Standard Mixtures A and B using Equation 10.



EQ. 10

$$\text{Resolution} = \frac{V}{H} \times 100$$

Where:

V = Depth of the valley between the two peaks. The depth of the valley is measured along a vertical line from the level of the apex of the shorter peak to the floor of the valley between the two peaks.

H = Height of the shorter of the adjacent peaks.

#### 9.2.5 Technical Acceptance Criteria for Initial Calibration

All initial calibration technical acceptance criteria apply independently to each GC column.

- 9.2.5.1 The initial calibration sequence must be analyzed according to the procedure and in the order listed in Section 9.2.3, at the concentrations listed in Section 7.2.3, and at the frequency listed in Section 9.2.2. The GC/ECD operating conditions optimized in Section 9.1 must be followed.
- 9.2.5.2 The resolution between two adjacent peaks in the Resolution Check Mixture must be greater than or equal to 60.0 percent.
- 9.2.5.3 All single component pesticides and surrogates in both runs of the PEM must be greater than or equal to 90.0 percent resolved on each column.
- 9.2.5.4 The absolute RTs of each of the single component pesticides and surrogates in both runs of the PEM must be within the RT window determined from the three-point initial calibration in Section 9.2.4.3.
- 9.2.5.5 The percent difference of the calculated amount (amount found) and the nominal amount (amount added) for each of the single component pesticides and surrogates in both of the PEM runs of each GC column must be greater than or equal to -25 percent and less than or equal to 25 percent using Equation 9.

- 9.2.5.6 The percent breakdown of DDT and endrin in each of the PEM runs must be less than or equal to 20.0 percent. The combined breakdown of DDT and endrin must be less than or equal to 30.0 percent.
- 9.2.5.7 The %RSD of the calibration factors for each single component target compound must be less than or equal to 20.0 percent, except alpha-BHC and delta-BHC. The %RSD of the calibration factors for alpha-BHC and delta-BHC must be less than or equal to 25.0 percent. The %RSD of the calibration factors for the two surrogates must be less than or equal to 30.0 percent. Up to two single component target compounds (not surrogates) per column may exceed the 20.0 percent limit for %RSD (25.0 percent for alpha-BHC and delta-BHC), but those compounds must have a %RSD of less than or equal to 30.0 percent.
- 9.2.5.8 The resolution between any two adjacent peaks in the midpoint concentrations of Individual Standard Mixtures A and B in the initial calibration must be greater than or equal to 90.0 percent.
- 9.2.5.9 All instrument blanks must meet the technical acceptance criteria in Section 12.1.4.5.
- 9.2.5.10 The identification of single component pesticides by gas chromatographic methods is based primarily on RT data. The RT of the apex of a peak can only be verified from an on-scale chromatogram. The identification of multicomponent analytes by gas chromatographic methods is based primarily on recognition of patterns of RTs displayed on a chromatogram. Therefore, the following requirements apply to all data presented for single component and multicomponent analytes.
- The chromatograms that result from the analyses of the Resolution Check Mixture, the PEM, and Individual Standard Mixtures A and B during the initial calibration sequence must display the single component analytes present in each standard at greater than 10 percent of full scale but less than 100 percent of full scale.
  - The chromatograms for at least one of the three analyses each of Individual Standard Mixtures A and B from the initial calibration sequence must display the single component analytes at greater than 50 percent and less than 100 percent of full scale.
  - The chromatograms of the standards for the multicomponent analytes analyzed during the initial calibration sequence must display the peaks chosen for identification of each analyte at greater than 25 percent and less than 100 percent of full scale.
  - For all Resolution Check Mixtures, PEMs, Individual Standard Mixtures, and blanks, the baseline of the chromatogram must return to below 50 percent of full scale before the elution time of alpha-BHC, and return to below 25 percent of full scale after the elution time of alpha-BHC and before the elution time of decachlorobiphenyl.
  - If a chromatogram is replotted electronically to meet requirements, the scaling factor used must be displayed on the chromatogram.

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- If the chromatogram of any standard needs to be replotted electronically to meet these requirements, both the initial chromatogram and the replotted chromatogram must be submitted in the data package.

9.2.6 Corrective Action for Initial Calibration

- 9.2.6.1 If the technical acceptance criteria for the initial calibration are not met, inspect the system for problems. It may be necessary to change the column, bake out the detector, clean the injection port, or take other corrective actions to achieve the technical acceptance criteria.
- 9.2.6.2 Contamination should be suspected as a cause if the detector cannot achieve acceptable linearity using this method. In the case of low level contamination, baking out the detector at elevated temperature (350°C) should be sufficient to achieve acceptable performance. In the case of heavy contamination, passing hydrogen through the detector for 1-2 hours at elevated temperature may correct the problem. In the case of severe contamination, the detector may require servicing by the ECD manufacturer. DO NOT OPEN THE DETECTOR. THE ECD CONTAINS RADIOCHEMICAL SOURCES.
- 9.2.6.3 If a laboratory cleans out a detector using elevated temperature, the ECD electronics must be turned off during the bake out procedure.
- 9.2.6.4 After bake out or hydrogen reduction, the detector must be recalibrated using the initial calibration sequence.
- 9.2.6.5 Initial calibration technical acceptance criteria MUST be met before any samples (including Laboratory Control Samples, matrix spike, and matrix spike duplicate, if required) or required blanks (method/sulfur clean-up) are analyzed. Any samples or required blanks analyzed when the initial calibration technical acceptance criteria have not been met will require re-analysis at no additional cost to USEPA.

9.3 Calibration Verification

9.3.1 Summary of Calibration Verification

Three types of analyses are used to verify the calibration and evaluate instrument performance. The analyses of instrument blanks, PEMs, and the mid point concentration of Individual Standard Mixtures A and B constitute the calibration verification. Sample (including Laboratory Control Sample and matrix spike and matrix spike duplicate, if required) and required blank (method/sulfur clean-up) data are not acceptable unless bracketed by acceptable analyses of instrument blanks, PEM, and both Individual Standard Mixtures A and B.

9.3.2 Frequency of Calibration Verification

- 9.3.2.1 An instrument blank and the PEM must bracket one end of a 12-hour period during which sample and required blank data are collected, and a second instrument blank and the mid point concentration of Individual Standard Mixtures A and B must bracket the other end of the 12-hour period.

- 9.3.2.2 For the 12-hour period immediately following the initial calibration sequence, the instrument blank and the PEM that are the last two steps in the initial calibration sequence bracket the front end of that 12-hour period. The injection of the instrument blank starts the beginning of the 12-hour period (Section 10.2.2.1). Samples [including Laboratory Control Samples (LCSs) and matrix spike and matrix spike duplicate (MS/MSD), if required] and required blanks (method/sulfur clean-up) may be injected for 12 hours from the injection of the instrument blank. The first three injections immediately after that 12-hour period must be an instrument blank, Individual Standard Mixture A, and Individual Standard Mixture B. The instrument blank must be analyzed first, before either standard. The Individual Standard Mixtures may be analyzed in either order (A,B or B,A).
- 9.3.2.3 The analyses of the instrument blank and Individual Standard Mixtures A and B immediately following one 12-hour period may be used to begin the subsequent 12-hour period, provided that they meet the technical acceptance criteria in Section 9.3.5. In that instance, the subsequent 12-hour period must be bracketed by the acceptable analyses of an instrument blank and a PEM, in that order. Those two analyses may in turn be used to bracket the front end of yet another 12-hour period. This progression may continue every 12 hours until such time as any of the instrument blanks, PEMs, or Individual Standard Mixtures fails to meet the technical acceptance criteria in Section 9.3.5. The 12-hour time period begins with the injection of the instrument blank.
- 9.3.2.4 Standards (PEM or Individual Standard Mixtures), samples and required blanks may be injected for 12 hours from the time of injection of the instrument blank.
- 9.3.2.5 If more than 12 hours have elapsed since the injection of the instrument blank that bracketed a previous 12-hour period, an acceptable instrument blank and PEM must be analyzed in order to start a new sequence. This requirement applies even if no analyses were performed since that standard was injected.
- 9.3.2.6 The requirements for running the instrument blanks, PEM, and Individual Standard Mixtures A and B are waived when no samples (including Laboratory Control Samples, requested matrix spike and matrix spike duplicate) dilutions, re-analyses, required blanks (method/sulfur clean-up), and multicomponent analytes for the 72-hour confirmation requirement are analyzed during that 12-hour period. To resume analysis, using the existing initial calibration, the Contractor must first analyze an instrument blank and PEM which meet the technical acceptance criteria.
- 9.3.2.7 If the entire 12-hour period is not required for the analyses of all samples and blanks to be reported and all data collection is to be stopped, the sequence must be ended with either the instrument blank/PEM combination or the instrument blank/Individual Standard Mixtures A and B combination, whichever was due to be performed at the end of the 12-hour period.
- 9.3.3 Procedure for Calibration Verification
- 9.3.3.1 All Standards and blanks must warm to ambient temperature prior to analysis.



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9.3.3.2 Analyze the instrument blank, PEM, and the mid point concentration of Individual Standard Mixtures A and B at the required frequencies (Section 9.3.2).

9.3.4 Calculations for Calibration Verification

9.3.4.1 For each analysis of the PEM used to demonstrate calibration verification, calculate the percent difference between the amount of each analyte (including the surrogates) found in the PEM and the nominal amount, using Equations 5 and 9.

9.3.4.2 For each analysis of the PEM used to demonstrate calibration verification, calculate the percent breakdown of Endrin and DDT, and the combined breakdown, using Equations 5, 6, 7, and 8.

9.3.4.3 For each analysis of the mid point concentration of Individual Standard Mixtures A and B used to demonstrate calibration verification, calculate the percent difference between the amount of each analyte (including the surrogates) found in the standard mixture and the nominal amount, using Equations 5 and 9. Do not attempt to calculate the breakdown of Endrin and DDT in the Individual Standard Mixtures, as these standards contain the breakdown products as well as the parent compounds.

9.3.5 Technical Acceptance Criteria For Calibration Verification

All calibration verification technical acceptance criteria apply independently to each GC column.

9.3.5.1 The PEMs, Individual Standard Mixtures, and instrument blanks must be analyzed at the required frequency (Section 9.3.2), on a GC/ECD system that has met the initial calibration technical acceptance criteria.

9.3.5.2 All single component pesticides and surrogates in the PEMs used to demonstrate calibration verification must be greater than or equal to 90.0 percent resolved. The resolution between any two adjacent peaks in the midpoint concentrations of Individual Standard Mixtures A and B used to demonstrate calibration verification must be greater than or equal to 90.0 percent.

9.3.5.3 The absolute RT for each of the single component pesticides and surrogates in the PEMs and mid point concentration of the Individual Standard Mixtures used to demonstrate calibration verification must be within the RT windows determined from the three-point initial calibration in Section 9.2.4.3.

9.3.5.4 The percent difference of the calculated amount (amount found) and the nominal amount (amount added) for each of the single component pesticides and surrogates in the PEM and midpoint concentration of the Individual Standard Mixtures used to demonstrate calibration verification must be greater than or equal to -25.0 percent and less than or equal to 25.0 percent.

9.3.5.5 The percent breakdown of 4,4'-DDT in the PEM must be less than or equal to 20.0 percent on each column. The percent breakdown of Endrin in the PEM must be less than or equal to 20.0 percent on each column. The combined breakdown of DDT and endrin must be less than or equal to 30.0 percent on each column.

9.3.5.6 All instrument blanks must meet the technical acceptance criteria in Section 12.1.4.5.

- 9.3.5.7 The identification of single component pesticides by gas chromatographic methods is based primarily on RT data. Since the RT of the apex of a peak can only be verified from an on-scale chromatogram, the following requirements must be met for calibration verification to be acceptable:
- The chromatograms that result from the analyses of the PEM and the Individual Standard Mixtures must display the single component analytes present in each standard at greater than 10 percent of full scale but less than 100 percent of full scale;
  - For any PEM, Individual Standard Mixture, or blank, the baseline of the chromatogram must return to below 50 percent of full scale before the elution time of alpha-BHC, and return to below 25 percent of full scale after the elution time of alpha-BHC and before the elution time of decachlorobiphenyl;
  - If a chromatogram is replotted electronically to meet these requirements, the scaling factor used must be displayed on the chromatogram; and
  - If the chromatogram of any standard or blank needs to be replotted electronically to meet these requirements, both the initial chromatogram and the replotted chromatogram(s) must be submitted in the data package.
- 9.3.6 Corrective Action for Calibration Verification
- 9.3.6.1 If the technical acceptance criteria for the calibration verification are not met, inspect the system for problems and take corrective action to achieve the technical acceptance criteria.
- 9.3.6.2 Major corrective actions such as replacing the GC column or baking out the detector will require that a new initial calibration be performed that meets the technical acceptance criteria in Section 9.2.5.
- 9.3.6.3 Minor corrective actions may not require performing a new initial calibration, provided that a new analysis of the standard (PEM or Individual Mixtures) that originally failed the criteria and an associated instrument blank immediately after the corrective action do meet all the technical acceptance criteria.
- 9.3.6.4 If a PEM or Individual Standard Mixture does not meet the technical acceptance criteria listed above, it must be reinjected immediately. If the second injection of the PEM or Individual Standard Mixture meets the criteria, sample analysis may continue. If the second injection does not meet the criteria, all data collection must be stopped. Appropriate corrective action must be taken, and a new initial calibration sequence must be run before more sample data are collected.
- 9.3.6.5 If an instrument blank does not meet the technical acceptance criteria listed in Section 12.1.4.5, all data collection must be stopped. Appropriate corrective action must be taken to clean out the system, and an acceptable instrument blank must be analyzed before more sample data are collected.
- 9.3.6.6 Analysts are reminded that running an instrument blank and a PEM or Individual Standard Mixtures once every 12 hours are the minimum contract requirements. Late eluting peaks may carry over from one injection to the next if highly complex samples are

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analyzed or if the GC conditions are unstable. Such carryover is unacceptable. Therefore, it may be necessary to run instrument blanks and standards more often to avoid discarding data.

- 9.3.6.7 If a successful instrument blank and PEM cannot be run after an interruption in analysis (Section 9.3.2.6), an acceptable initial calibration must be run before sample data may be collected. All acceptable sample (including Laboratory Control Samples, requested matrix spike and matrix spike duplicate) and required blank (method/sulfur clean-up) analyses must be preceded and followed by acceptable standards and instrument blanks, as described in Section 9.3.2.
- 9.3.6.8 Calibration verification technical acceptance criteria must be met before any samples (including the Laboratory Control Sample, requested matrix spike and matrix spike duplicate) and required blanks (method/sulfur clean-up) are reported. Any samples and required blanks associated with a calibration verification which did not meet the technical acceptance criteria will require re-analysis at no additional cost to USEPA.

10.0 PROCEDURE

10.1 Sample Preparation

10.1.1 This method is designed for analysis of water samples that contain low concentrations of the pesticides and Aroclors listed in Exhibit C. The majority of the samples are expected to come from drinking water and well/ground water type sources around Superfund sites. If, upon inspection of a sample, the Contractor suspects that the sample is not amenable to this method, contact Sample Management Office (SMO). SMO will contact the Region for instructions.

10.1.2 If insufficient sample volume (less than 90 percent of the required amount) is received to perform the analyses, the Contractor shall contact SMO to apprise them of the problem. SMO will contact the Region for instructions. The Region will either require that no sample analyses be performed or will require that a reduced volume be used for the sample analysis. No other changes in the analyses will be permitted. The Contractor shall document the Region's decision in the Sample Delivery Group (SDG) Narrative.

10.1.3 Extraction of Samples

Water samples may be extracted by either separatory funnel procedure or a continuous liquid-liquid extraction procedure. If an emulsion prevents acceptable solvent recovery with the separatory funnel procedure, continuous liquid-liquid extraction must be employed. Allow the samples to come to ambient temperature (approximately one hour).

10.1.3.1 Separatory Funnel Extraction

10.1.3.1.1 Measure out each 1 L sample aliquot in a separate graduated cylinder. Measure and record the pH of the sample with wide range pH paper and adjust the pH to between 5 and 9 with 10 N sodium hydroxide or concentrated sulfuric acid, if required. Samples requiring pH adjustment must be noted in the SDG narrative. Place the sample aliquot into a 2 L separatory funnel.

10.1.3.1.2 Using a syringe or a volumetric pipet add 200 microliter ( $\mu$ L) of the surrogate solution (Section 7.2.3.1) to all water samples.

10.1.3.1.3 Rinse the graduated cylinder with 30 milliliters (mL) of methylene chloride and transfer the rinsate to the separatory funnel. If the sample container is empty, rinse the container with 30 mL of methylene chloride and add the rinsate to the separatory funnel. If the sample container is not rinsed, then add another 30 mL of methylene chloride to the separatory funnel and extract the sample by shaking the funnel for two minutes, with periodic venting to release excess pressure.

NOTE: The total volume of solvent used for extraction is 60 mL. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, and may include stirring, filtration through glass wool, centrifugation or other physical means. Drain the methylene chloride into a 250 mL Erlenmeyer flask.

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10.1.3.1.4 Add a second 60 mL volume of methylene chloride to the separatory funnel and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner.

10.1.3.2 Continuous Liquid-Liquid Extraction

10.1.3.2.1 Continuous Liquid-Liquid Extraction Without Hydrophobic Membrane

10.1.3.2.1.1 Follow manufacturer's instructions for set-up.

10.1.3.2.1.2 Add methylene chloride to the bottom of the extractor and fill it to a depth of at least one inch above the bottom sidearm.

10.1.3.2.1.3 Measure out each 1 L sample aliquot in a separate, clean graduated cylinder; transfer the aliquot to the continuous extractor. Measure the pH of the sample with wide range pH paper or pH meter and record pH. Adjust the pH to between 5 and 9 with 10 N sodium hydroxide or concentrated sulfuric acid, as required. Samples requiring the pH adjustment must be noted in the SDG Narrative.

NOTE: With some samples, it may be necessary to place a layer of glass wool between the methylene chloride and the water layer in the extractor to prevent precipitation of suspended solids into the methylene chloride during extraction.

10.1.3.2.1.4 Using a syringe or volumetric pipet, add 200 µL of the surrogate standard spiking solution (Section 7.2.3.1) into the sample and mix well.

10.1.3.2.1.5 Rinse the graduated cylinder with 50 mL of methylene chloride and transfer the rinsate to the continuous extractor. If the sample container is empty, rinse the container with 50 mL of methylene chloride and add the rinsate to the continuous extractor.

10.1.3.2.1.6 Add sufficient methylene chloride to the continuous extractor to ensure proper solvent cycling during operation. Adjust the drip rate to 5 to 15 mL/minute (recommended); optimize the extraction drip rate. Extract for a minimum of 18 hours.

NOTE 1: When a minimum drip rate of 10-15 mLs/minute is maintained throughout the extraction, the extraction time may be reduced to a minimum of 12 hours. Allow to cool, then detach the distillation flask. Proceed to Section 10.1.4.

NOTE 2: Some continuous liquid-liquid extractors are also capable of concentrating the extract within the extraction set-up. Follow the manufacturer's instructions for concentration when using this type of extractor.

10.1.3.2.2 Continuous Liquid-Liquid Extraction With Hydrophobic Membrane

10.1.3.2.2.1 Follow the manufacturer's instructions for set-up.

10.1.3.2.2.2 Measure out each 1 L sample aliquot in a separate, clean graduated cylinder. If the sample container is empty, rinse the container with 50 mL of methylene chloride and add the rinsate to the continuous extractor. If the sample was not received in a 1 L container, add 50 mL of methylene chloride to the continuous extractor. Slowly transfer the aliquot to the continuous extractor. Measure the pH of the sample with wide range pH paper or pH meter and record pH. Adjust the pH to between 5 and 9 with 10 N sodium hydroxide or concentrated sulfuric acid, as required. Samples requiring the pH adjustment must be noted in the SDG Narrative.

10.1.3.2.2.3 Using a syringe or volumetric pipet, add 200  $\mu$ L of the surrogate standard spiking solution (Section 7.2.3.1) into the sample and mix well.

10.1.3.2.2.4 Rinse the graduated cylinder with 50 mL of methylene chloride and transfer the rinsate to the continuous extractor.

10.1.3.2.2.5 Add sufficient methylene chloride to the continuous extractor to ensure proper solvent cycling during operation. Adjust the drip rate to 15 mL/minute (recommended); optimize the extraction drip rate. Extract for a minimum of 6 hours.

NOTE 1: Due to the smaller volume of solvent used during the extraction process, some sample matrices (e.g., oily samples, samples containing a high concentration of surfactants) may create an emulsion which will consume the solvent volume, preventing the efficient extraction of the sample. When this occurs, add additional solvent to ensure efficient extraction of the sample, and extend the extraction time for a minimum of 6 hours. If the sample matrix prevents the free flow of solvent through the membrane, then the non-hydrophobic membrane continuous liquid-liquid type extractor must be used.

Allow to cool, then detach the distillation flask. Proceed to Section 10.1.4.

NOTE 2: Some continuous liquid-liquid extractors are also capable of concentrating the extract within the extraction set-up. Follow the manufacturer's instructions for concentration when using this type of extractor. Using the hydrophobic membrane, it may not be necessary to dry the extract with sodium sulfate.

NOTE 3: If low surrogate recoveries occur, assure 1) the apparatus was properly assembled to prevent leaks; 2) the drip rate/solvent cycling was optimized; and 3) there was proper cooling for condensation of solvent. Document the problem and the corrective action.

NOTE 4: Alternate continuous liquid-liquid extractor types that meet the requirements of the SOW may also be used. If using alternate extractors or design types, follow the manufacturer's instructions for set-up. Optimize the extraction procedure.

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10.1.4 Extract Drying and Concentration

- 10.1.4.1 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10 mL concentrator tube to a 500 mL evaporative flask. Other concentration devices or techniques may be used in place of the K-D, if equivalency is demonstrated for all the target pesticides and Aroclors listed in Exhibit C.
- 10.1.4.1 Pour the extract through a drying column containing about 10 centimeters (cm) of anhydrous granular sodium sulfate and collect the extract in the K-D concentrator. Rinse the Erlenmeyer flask and the sodium sulfate with at least two additional 20 to 30 mL portions of methylene chloride to complete the quantitative transfer.
- 10.1.4.3 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (60-90°C recommended) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 30 minutes. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 3 to 5 mL, remove the K-D apparatus. Allow it to drain and cool for at least 10 minutes. DO NOT ALLOW THE EVAPORATOR TO GO DRY. Proceed with the solvent exchange to hexane.
- 10.1.4.4 Solvent Exchange to Hexane
- 10.1.4.4.1 Momentarily remove the three-ball Snyder column, add 50 mL of hexane and a new boiling chip, and reattach the Snyder column. Pre-wet the column by adding about 1 mL of hexane to the top. Concentrate the solvent extract as before. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes. DO NOT ALLOW THE EVAPORATOR TO GO DRY.
- 10.1.4.4.2 Remove the Snyder column; using 1 to 2 mL of hexane, rinse the flask and its lower joint into the concentrator tube.
- 10.1.4.4.3 Use the micro Snyder column or the nitrogen blowdown technique to concentrate the hexane extract to 2.0 mL.
- 10.1.4.5 Final Concentration of Extract
- Two different techniques are permitted to concentrate the extract to 2.0 mL. They are the micro Snyder column and nitrogen evaporation techniques.
- 10.1.4.5.1 Micro Snyder Column Technique
- Add another one or two clean boiling chips to the concentrator tube and attach a two-ball micro Snyder column. Pre-wet the Snyder column by adding about 0.5 mL of hexane to the top of the column. Place the K-D apparatus in a hot water bath (80°C to 90°C recommended) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5 to 10 minutes. At the proper rate of

distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches about 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain for at least 10 minutes while cooling. Remove the Snyder column and rinse its flask and lower joint into the concentrator tube with 0.2 mL of hexane. Adjust the final volume with hexane to 2.0 mL.

- 10.1.4.5.2 Nitrogen Evaporation Technique (taken from ASTM Method D 3086).
- 10.1.4.5.2.1 Place the concentrator tube with an open micro Snyder column attached in a warm water bath (30°C to 35°C recommended) and evaporate the solvent volume to just below 1 or 2 mL by blowing a gentle stream of clean, dry nitrogen filtered through a column of activated carbon above the solvent. Adjust the final volume with hexane to 1.0 mL (Florisil cartridge check) or 2.0 mL (sample extract).
- 10.1.4.5.2.2 **CAUTION:** Gas lines from the gas source to the evaporation apparatus must be stainless steel, copper, or PTFE tubing. Plastic tubing must not be used between the carbon trap and the sample as it may introduce interferences. The internal wall of new tubing must be rinsed several times with hexane and then dried prior to use.
- 10.1.4.5.2.3 During evaporation, the tube solvent level must be kept below the water level of the bath. DO NOT ALLOW THE EXTRACT TO GO TO DRYNESS.
- 10.1.4.6 Proceed to Section 10.1.5 for extract cleanup. Otherwise, transfer the extract to a PTFE-lined screw-cap bottle and label the bottle. Store at 4°C (±2°C) but not greater than 6°C.
- 10.1.5 Extract Cleanup
  - 10.1.5.1 The two cleanup procedures specified in this method are Florisil cartridge and sulfur cleanup. Florisil cartridge cleanup is required for all extracts. Sulfur cleanup must be performed on all extracts containing sulfur at levels that interfere with Gas Chromatograph/Electron Capture Detector (GC/ECD) analysis. Sulfur contamination in a sample analysis is unacceptable. Method blanks must be subjected to the same cleanup procedures as the samples.
  - 10.1.5.2 Florisil Cleanup
    - 10.1.5.2.1 Introduction

Florisil cartridge cleanup significantly reduces matrix interference caused by polar compounds and is required for all extracts. The same volume of the concentrated extract taken for Florisil cleanup must be maintained after Florisil cleanup (2 mL).
    - 10.1.5.2.2 Florisil Cartridge Performance Check
      - 10.1.5.2.2.1 Summary of Florisil Cartridge Performance Check

Every lot number of Florisil cartridges must be tested before they are used for sample cleanup.



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10.1.5.2.2.2 Frequency of Florisil Cartridge Performance Check

Cartridge performance check must be conducted at least once on each lot of cartridges used for sample cleanup or every 6 months whichever is most frequent.

10.1.5.2.2.3 Procedure for Florisil Cartridge Performance Check

Add 0.5 mL of 2,4,5-trichlorophenol solution (0.1 µg/mL in acetone, Section 7.2.3.7) and 0.5 mL of Standard Mixture A, midpoint concentration, Section 7.2.3.5) to 4 mL of hexane. Reduce the volume to 0.5 mL using nitrogen (Section 10.1.4.5.2). Place the mixture onto the top of a washed Florisil cartridge, and elute it with 9 mL of hexane/acetone [(90:10)(V/V)]. Use two additional 1 mL hexane rinses to ensure quantitative transfer of standard from the cartridge. Concentrate to a final volume of 1 mL and analyze the solution by GC/ECD using at least one of the GC columns specified for sample analysis. Determine the recovery of each analyte for evaluation and reporting purposes. Calculate the percent recovery using Equation 11.

EQ. 11

$$\text{Percent Recovery} = \frac{Q_d}{Q_a} \times 100$$

Where:

$Q_d$  = Quantity determined by analysis.

$Q_a$  = Quantity added.

10.1.5.2.2.4 Technical Acceptance Criteria for Florisil Cartridge Performance Check

10.1.5.2.2.4.1 The cartridge performance check solution must be analyzed on a GC/ECD meeting the initial calibration and calibration verification technical acceptance criteria.

10.1.5.2.2.4.2 The lot of Florisil cartridges is acceptable if all pesticides are recovered at 80 to 120 percent, if the recovery of trichlorophenol is less than 5 percent, and if no peaks interfering with the target analytes are detected.

10.1.5.2.2.5 Corrective Action for Florisil Cartridge Performance Check

Any lot of Florisil cartridges that does not meet the criteria above must be discarded and a new lot, meeting criteria, used for sample cleanup.

10.1.5.2.3 Sample Cleanup by Florisil Cartridge

The required Florisil cartridge size is a 1 g cartridge and the final volume of the extract after Florisil cleanup is 2 mL.

10.1.5.2.3.1 Frequency of Sample Cleanup by Florisil Cartridge

All sample extracts (including Laboratory Control Samples and requested matrix spike and matrix spike duplicate) and method blank extracts are required to be cleaned up by the Florisil cartridge technique.

10.1.5.2.3.2 Procedure for Sample Cleanup by Florisil Cartridge

10.1.5.2.3.2.1 Attach the vacuum manifold to a water aspirator or to a vacuum pump with a trap installed between the manifold and the vacuum source. Adjust the vacuum pressure in the manifold to between 5 and 10 pounds of vacuum.

10.1.5.2.3.2.2 Place one Florisil cartridge into the vacuum manifold for each sample extract.

10.1.5.2.3.2.3 Prior to cleanup of samples, the cartridges must be washed with hexane/acetone (90:10). This is accomplished by placing the cartridge on the vacuum manifold, by pulling a vacuum, and by passing at least 5 mL of the hexane/acetone solution through the cartridge. While the cartridges are being washed, adjust the vacuum applied to each cartridge so that the flow rate through each cartridge is approximately equal. DO NOT ALLOW THE CARTRIDGES TO GO DRY AFTER THEY HAVE BEEN WASHED.

10.1.5.2.3.2.4 After the cartridges on the manifold are washed, the vacuum is released, and a rack containing labeled 10 mL volumetric flasks is placed inside the manifold. Care must be taken to ensure that the solvent line from each cartridge is placed inside of the appropriate volumetric flask as the manifold top is replaced.

10.1.5.2.3.2.5 After the volumetric flasks are in place, the vacuum to the manifold is restored, and a volume of extract equal to the required final volume from each sample and method blank extract is transferred to the top frit of the appropriate Florisil cartridge. This must equal the final volume after Florisil cleanup.

10.1.5.2.3.2.6 Because the volumes marked on concentrator tubes are not necessarily accurate at the 1 mL level, the use of a syringe or a volumetric pipet is required to transfer the extract to the cleanup cartridge.

10.1.5.2.3.2.7 The pesticides/Aroclors in the extract concentrates are then eluted through the column with 8 mL of hexane/acetone (90:10) and are collected into the 10 mL volumetric flasks held in the rack inside the vacuum manifold.

10.1.5.2.3.2.8 Transfer the eluate in each volumetric flask to a clean centrifuge tube or 10 mL vial. Use two additional 1 mL hexane rinses to ensure quantitative transfer of the cartridge eluate.

10.1.5.2.3.2.9 Adjust the extract to 2 mL aliquot volume as was taken for cleanup using either nitrogen blowdown or a micro Snyder column (Section 10.1.4.5). Measure the final volume with a syringe or by transferring the extract to a volumetric flask.

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10.1.5.2.3.2.10            If sulfur cleanup is to be performed, proceed to Section 10.1.5.3.3. Otherwise, transfer the sample to a GC vial and label the vial. The extract is ready for GC/ECD analysis.

10.1.5.3            Sulfur Cleanup

10.1.5.3.1            Introduction

10.1.5.3.1.1            Sulfur contamination will cause a rise in the baseline of a chromatogram and may interfere with the analyses of the later eluting pesticides. If crystals of sulfur are evident or if the presence of sulfur is suspected, sulfur removal must be performed. Interference which is due to sulfur is not acceptable. Sulfur can be removed by one of two methods, according to laboratory preference. If the sulfur concentration is such that crystallization occurs in the concentrated extract, centrifuge the extract to settle the crystals, and remove the sample extract with a disposable pipette, leaving the excess sulfur in the centrifuge tube. Transfer the extract to a clean centrifuge tube or clean concentrator tube before proceeding with further sulfur cleanup.

10.1.5.3.1.2            If only part of a set of samples require sulfur cleanup, then, a sulfur cleanup blank is required for that part of the set (Section 12.1.3.2).

10.1.5.3.2            Frequency of Sulfur Cleanup

Sulfur removal is required for all sample extracts that contain sulfur.

10.1.5.3.3            Procedure for Sulfur Cleanup

10.1.5.3.3.1            Mercury Technique

Add one to three drops of mercury to each hexane extract in a clean vial. Tighten the top on the vial and agitate the sample for 30 seconds. Filter or centrifuge the extract. Pipet the extract to another vial and leave all solid precipitate and liquid mercury. If the mercury appears shiny, proceed to Section 10.2 and analyze the extract. If the mercury turns black, repeat sulfur removal as necessary. The extract transferred to the vial still represents the 2.0 mL final volume. CAUTION: Waste containing mercury should be segregated and disposed of properly.

NOTE: Mercury is a highly toxic metal and therefore must be used with great care. Prior to using mercury, it is recommended that the analyst become acquainted with proper handling and cleanup techniques associated with this metal.

10.1.5.3.3.2            Copper Technique

Add approximately 2 grams (g) of cleaned copper powder to the extract in the centrifuge or concentrator tube (2 g will fill the tube to about the 0.5 mL mark). Mix the copper and extract for at least 1 minute on a mechanical shaker. Separate the extract from the copper powder by drawing off the extract with a disposable pipet, and transfer the extract to a clean vial. The extract transferred to the

vial still represents the 2.0 mL final volume. The separation of the extract from the copper powder is necessary to prevent degradation of the pesticides. If the copper appears bright, proceed to Section 10.2 and analyze the extracts. If the copper changes color, repeat the sulfur removal procedure as necessary.

## 10.2 GC Analysis

### 10.2.1 Introduction

10.2.1.1 Before samples (including Laboratory Control Samples and requested matrix spike and matrix spike duplicate) and required blanks (method/sulfur clean-up) can be analyzed, the instrument must meet the initial calibration and calibration verification technical acceptance criteria. All sample extracts, required blanks, and calibration standards must be analyzed under the same instrumental conditions. All sample extracts, required blank extracts, and standard/spiking solutions must be allowed to warm to ambient temperature (approximately 1 hour) before preparation/analysis. Sample analysis on both GC columns is required for all samples and blanks.

10.2.1.2 Set up the GC/ECD system per the requirements in Section 9.1. Unless ambient temperature on-column injection is used (Section 9.1), the injector must be heated to at least 200°C. The optimized gas chromatographic conditions from Section 9.1 must be used.

### 10.2.2 Procedure for Sample Analysis by GC/ECD

The injection must be made on-column by using either automatic or manual injection. If autoinjectors are used, 1.0 µL injection volumes may be used. Manual injections must use at least 2.0 µL injection volumes. The same injection volume must be used for all standards, samples, and blanks associated with the same initial calibration. If a single injection is used for two GC columns attached to a single injection port, it may be necessary to use an injection volume greater than 2 µL. However, the same injection volume must be used for all analyses.

#### 10.2.2.1 Analytical Sequence

All samples and required blanks must be analyzed within a valid analysis sequence as given below.

<u>Time</u>	<u>Injection #</u>	<u>Material Injected</u>
0 hr.	1-15	First 15 steps of the initial calibration
	16	Instrument blank at end of initial calibration
	17	PEM at end of initial calibration
	18	First sample
	0	Subsequent samples
	0	
12 hr.	0	
	0	Last sample

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<u>Time</u>	<u>Injection #</u>	<u>Material Injected</u>
	1st injection past 12:00 hr.	Instrument blank
	2nd and 3rd injections past 12:00 hr.	Individual Standard Mixtures A and B
	0	Sample
	0	
	0	Subsequent samples
	0	
	0	
Another 12 hr.	0	Last sample
	1st injection past 12 hr.	Instrument blank
	2nd injection	PEM
	0	Sample
	0	
	0	Subsequent samples
	0	
	0	
Another 12 hr.	0	Last sample
	1st injection past 12:00 hr.	Instrument blank
	2nd and 3rd injections past 12:00 hr.	Individual Standard Mixtures A and B
	0	Sample
	0	
	0	Subsequent samples
	0	
	0	
	etc.	

10.2.2.1.1 The first 12 hours are counted from injection #16 (the Instrument Blank at the end of the initial calibration sequence), not from injection #1. Samples and required blanks may be injected until 12:00 hours have elapsed. All subsequent 12-hour periods are timed from the injection of the instrument blank that brackets the front end of the samples. Because the 12-hour time period is timed from injection of the instrument blank until the injection of the last sample, each 12-hour period may be separated by the length of one chromatographic run, that of the analysis of the last sample. While the 12-hour period may not be exceeded, the laboratory may run instrument blanks and standards more frequently, for instance, to accommodate staff working on 8-hour shifts.

10.2.2.1.2 After the initial calibration, the analysis sequence may continue as long as acceptable instrument blanks, PEMs and Individual Standard Mixtures A and B are analyzed at the required frequency. This analysis sequence shows only the minimum required blanks and standards. More blanks and standards may be run at the discretion of the Contractor; however, the blanks and standards must also satisfy the

criteria presented in Section 9 in order to continue the run sequence.

- 10.2.2.1.3        An analysis sequence must also include all samples and required blank analyses, but the Contractor may decide at what point in the sequence they are to be analyzed.
- 10.2.2.1.4        The requirements for the analysis sequence apply to each GC column and for all instruments used for these analyses.
- 10.2.3        Sample Dilutions
- 10.2.3.1        The sample must first be analyzed at the most concentrated level (injection taken from the 2.0 mL final extract after the clean-up steps).
- 10.2.3.2        If the concentration of any single component pesticide is greater than the upper limit of the initial calibration range on both GC columns, then the extract must be diluted. If the concentration of any single component pesticide is greater than the upper limit of the initial calibration range on one GC column, but not the other, then the extract must be diluted only if the percent difference between the two concentrations is less than or equal to 25%. The on-column concentration of the pesticide compound(s) in the diluted extract must be between the initial calibration low point and high point standards.
- 10.2.3.3        If the calculated concentration of any multicomponent peak, used for quantitation is greater than the concentration of the most intense single component analyte in the initial calibration high point standard, then the sample must be diluted to have the concentration of the largest peak in the multicomponent analyte between the initial calibration midpoint and high point standards of that single component pesticide.
- 10.2.3.4        If dilution is employed solely to bring a peak within the calibration range or to get a multicomponent pattern on scale, the results for both the more and the less concentrated extracts must be reported. The resulting changes in quantitation limits and surrogate recovery must be reported also for the diluted samples.
- 10.2.3.5        If the dilution factor is greater than 10, an additional extract 10 times more concentrated than the diluted sample extract must be analyzed and reported with the sample data. If the dilution factor is less than 10, but greater than 1, the results of the original undiluted analysis must also be reported.
- 10.2.3.6        If the analysis of the most concentrated extract does not meet the requirement for dilution in Section 10.2.3.2 and 10.2.3.3, then the analysis is at no additional cost to USEPA.
- 10.2.3.7        When diluted, the chromatographic data for the single component pesticide must be able to be reported at greater than 10 percent of full scale but less than 100 percent of full scale.
- 10.2.3.8        When diluted, multicomponent analytes must be able to be reported at greater than 25 percent of full scale but less than 100 percent of full scale.
- 10.2.3.9        If a chromatogram is replotted electronically to meet these requirements, the scaling factor used must be displayed on the chromatogram. If the chromatogram of any sample needs to be replotted electronically to meet these requirements, both the

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initial chromatogram and the replotted chromatogram(s) must be submitted in the data package.

10.2.3.10 Dilute the sample using the following procedure:

10.2.3.10.1 Calculate the extract dilution in order for the single component pesticides to meet the requirement listed in Section 10.2.3.7.

10.2.3.10.2 Calculate the extract dilution in order for the multicomponent analytes to meet the requirement listed in Section 10.2.3.8.

10.2.3.10.3 Dilute the sample extract quantitatively with hexane.

## 11.0 DATA ANALYSIS AND CALCULATIONS

### 11.1 Qualitative Identification of Target Compounds

- 11.1.1 The laboratory will identify single component analyte peaks based on the Retention Time (RT) windows established during the initial calibration sequence. Single component analytes are identified when peaks are observed in the RT window for the analyte on both Gas Chromatograph (GC) columns.
- 11.1.2 A set of three to five major peaks is selected for each multicomponent analyte. RT windows for each peak are determined from the initial calibration analysis. Identification of a multicomponent analyte in the sample is based on pattern recognition in conjunction with the elution of three to five sample peaks within the RT window of the corresponding peaks of the standard on both GC columns. The number of potential quantitation peaks is listed in Table D-2.
- 11.1.3 A standard of any identified multicomponent analyte must be run within 72 hours of its detection in a sample chromatogram within a valid 12-hour sequence.
- 11.1.4 The choice of the peaks used for multicomponent analyte identification and the recognition of those peaks may be complicated by the environmental alteration of the toxaphene or Aroclors, and by the presence of coeluting analytes, or matrix interferences, or both. Because of the alteration of these materials in the environment, multicomponent analytes in samples may give patterns similar to, but not identical with, those of the standards.
- 11.1.5 Toxaphene and Aroclors require only a single-point calibration. Identification requires visual inspection of an on-scale pattern.

### 11.2 Calculations

#### 11.2.1 Target Compounds

- 11.2.1.1 Quantitation for all analytes and surrogates must be performed and reported for each GC column.
- 11.2.1.2 Manual integration of peaks (e.g., measuring peak height with a ruler) is only permitted when accurate electronic integration of peaks cannot be done. If manual integration of peaks is required, it must be documented in the Sample Delivery Group (SDG) Narrative.
- 11.2.1.3 The Contractor must quantitate each single component analyte and surrogate based on the calibration factor from the most recent initial calibration midpoint standard mixture analyses. Do not use the analyses of the Individual Standard Mixtures used to demonstrate calibration verification for quantitation of samples.
- 11.2.1.4 The Contractor must quantitate each multicomponent analyte based on the calibration factor from the most recent initial calibration standard.
- 11.2.1.5 If more than one multicomponent analyte is present, the Contractor must choose separate peaks to quantitate the different multicomponent analytes. A peak common to both analytes present in the sample must not be used to quantitate either analyte.



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- 11.2.1.6 Before reporting data to USEPA, it is required that the Contractor check for flags generated by the data system that indicate improper quantitation of analytes.
- 11.2.1.7 The chromatograms of all samples (including Laboratory Control Samples, requested matrix spike/matrix spike duplicate) standards, and required blanks must be reviewed by a qualified pesticide analyst before they are reported.
- 11.2.1.8 Calculate the concentration of the single component pesticides and surrogates by using the following equation:

EQ. 12

$$\text{Concentration } \mu\text{g/L} = \frac{(A_x) (V_x) (Df)}{CF_{mp} (V_i) (V_x)}$$

Where:

- $A_x$  = Response (peak area or height) of the compound to be measured.
- $CF_{mp}$  = Calibration factor for the mid-point from initial calibration standard (area per ng).
- $V_t$  = Volume of concentrated extract ( $\mu\text{L}$ ). (This volume is 2000  $\mu\text{L}$ ).
- $V_i$  = Volume of extract injected ( $\mu\text{L}$ ). (If a single injection is made onto two columns, use one-half the volume in the syringe as the volume injected onto each column).
- $V_x$  = Volume of water extracted (mL). (NOTE: for instrument blanks and sulfur cleanup blanks, assume a 1,000 mL volume).
- $Df$  = Dilution factor. The dilution factor for analysis of water samples by this method is defined as follows:

$$\frac{\mu\text{L most concentrated extract used to make dilution} + \mu\text{L clean solvent}}{\mu\text{L most concentrated extract used to make dilution}}$$

If no dilution is performed,  $Df = 1.0$ .

The calibration factors used in Equation 12 are those from the most recent mid-point standard from the initial calibration. If the calibration factors used to determine the linearity of the initial calibration were based on peak area, then the concentration of the analyte in the sample must be based on peak area. Similarly, if peak height was used to determine linearity, use peak height to determine the concentration in the sample.

- 11.2.1.9 Contract Required Quantitation Limit (CRQL) Calculation
- If the adjusted CRQL is less than the CRQL listed in Exhibit C (Pesticides), report the CRQL in Exhibit C (Pesticides). Calculate the adjusted CRQL for pesticides by using the following equation:

EQ. 13

$$\text{Adjusted CRQL} = \text{Contract CRQL} \times \frac{\text{Contract Sample Vol (1000 mL)}}{V_x} \times Df \times \frac{V_t}{\text{Contract Ext. Vol (2000uL)}}$$

Where:

Contract CRQL = Take exact CRQL values reported in Exhibit C of the SOW.

$V_x$  = Same as EQ. 12.

$V_t$  = Same as EQ. 12.

Df = Same as EQ. 12.

11.2.1.10 During initial calibration, a set of three to five quantitation peaks was chosen for each multicomponent analyte. Calculate the concentration of each of the selected Aroclor or toxaphene peaks individually using Equation 12. Determine the mean concentration for all of the selected peaks. The mean value is reported on Form X (Exhibit B) for both GC columns.

11.2.1.11 For the single component pesticides, report the lower of the two values quantitated from the two GC columns of Form I. For the multicomponent analytes, report the lower of the two mean values from the two GC columns on Form I.

11.2.1.12 The percent difference is calculated according to Equation 14.

EQ. 14

$$PD = \frac{\text{Conc}_H - \text{Conc}_L}{\text{Conc}_L} \times 100$$

Where:

$\text{Conc}_H$  = The higher of the two concentrations for the target compound in question.

$\text{Conc}_L$  = The lower of the two concentrations for the target compound in question.

NOTE: Using this equation will result in percent difference values that are always positive. The value will also be greater than a value calculated using the higher concentration in the denominator, however, given the likelihood of a positive interference raising the concentration determined on one GC column, this is a conservative approach to comparing the two concentrations.

11.2.2 Surrogate Recoveries

11.2.2.1 The concentrations of the surrogates are calculated separately for each GC column in a similar manner as the other analytes using Equation 12. Use the calibration factors from the midpoint concentration of Individual Standard Mixture A from the initial calibration.

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- 11.2.2.2 The recoveries of the surrogates are calculated according to Equation 15.

EQ. 15

$$\text{Percent Recovery} = \frac{Q_d}{Q_a} * 100$$

Where:

$Q_d$  = Quantity determined by analysis.

$Q_a$  = Quantity added to sample/blank.

11.3 Technical Acceptance Criteria for Sample Analyses

The requirements below apply independently to each GC column and to all instruments used for these analyses. (See exception in Section 11.3.7) Quantitation must be performed on each GC column.

- 11.3.1 Samples must be analyzed under the Gas Chromatograph/Electron Capture Detector (GC/ECD) operating conditions in Section 9.1. The instrument must have met all initial calibration and calibration verification technical acceptance criteria. Samples must be cleaned-up using Florisil that meets the technical acceptance criteria for Florisil. Sample data must be bracketed at 12-hour intervals (or less) by acceptable analyses of instrument blanks, Performance Evaluation Mixtures (PEMs), and Individual Standard Mixtures A and B, as described in Section 10.2.2.1.
- 11.3.2 The sample must be extracted and analyzed within the contract holding times.
- 11.3.3 The Laboratory Control Sample (LCS) associated with the samples must meet the LCS technical acceptance criteria.
- 11.3.4 The samples must have an associated method blank meeting the method blank technical acceptance criteria. If a sulfur cleanup blank is associated with the samples, that blank must meet the sulfur cleanup blank technical acceptance criteria.
- 11.3.5 The RT for each of the surrogates must be within the RT window as calculated in Section 9.2.4.3, for both GC columns.
- 11.3.6 The percent recovery for the surrogates must be between 30.0 and 150 percent, inclusive. These limits are not advisory.
- NOTE: The surrogate recovery requirements do not apply to a sample that has been diluted.
- 11.3.7 No target analyte concentrations may exceed the upper limit of the initial calibration or else extracts must be diluted and re-analyzed. If a target analyte concentration exceeds the upper limit of the initial calibration on one GC column, but not the other, the extract must be diluted and re-analyzed only if the percent difference between the two concentrations is less than or equal to 25%.
- 11.3.8 A standard for any identified multicomponent analyte must be analyzed on the same instrument within 72 hours of its detection in a sample within a valid 12 hour sequence.

- 11.3.9 The identification of single component pesticides by gas chromatographic methods is based primarily on RT data. The RT of the apex of a peak can only be verified from an on-scale chromatogram. The identification of multicomponent analytes by gas chromatographic methods is based primarily on recognition of patterns of RTs displayed on a chromatogram. Therefore, the following requirements apply to all data presented for single component and multicomponent analytes.
- 11.3.9.1 When no analytes are identified in a sample, the chromatograms from the analyses of the sample extract must use the same scaling factor as was used for the low point standard of the initial calibration associated with those analyses.
- 11.3.9.2 Chromatograms must display single component pesticides detected in the sample at less than full scale.
- 11.3.9.3 Chromatograms must display the largest peak of any multicomponent analyte detected in the sample at less than full scale.
- 11.3.9.4 If an extract must be diluted, chromatograms must display single component pesticides between 10 and 100 percent of full scale.
- 11.3.9.5 If an extract must be diluted, chromatograms must display multicomponent analytes between 25 and 100 percent of full scale.
- 11.3.9.6 For any sample or blank, the baseline of the chromatogram must return to below 50 percent of full scale before the elution time of alpha-BHC, and return to below 25 percent of full scale after the elution time of alpha-BHC and before the elution time of decachlorobiphenyl.
- 11.3.9.7 If a chromatogram is replotted electronically to meet these requirements, the scaling factor used must be displayed on the chromatogram.
- 11.3.9.8 If the chromatogram of any sample needs to be replotted electronically to meet these requirements, both the initial chromatogram and the replotted chromatogram(s) must be submitted in the data package.
- 11.4 Corrective Action for Sample Analysis
- 11.4.1 Sample analysis technical acceptance criteria MUST be met before data are reported. Samples contaminated from laboratory sources or associated with a contaminated method blank or sulfur cleanup blank will require re-extraction and re-analysis at no additional cost to USEPA. Any samples analyzed that do not meet the technical acceptance criteria will require re-extraction and/or re-analysis at no additional cost to USEPA.
- 11.4.2 If the sample analysis technical acceptance criteria are not met, check calculations, surrogate solutions, and instrument performance. It may be necessary to recalibrate the instrument or take other corrective action procedures to meet the technical acceptance criteria, in which case, the affected samples must be re-analyzed at no additional cost to USEPA after the corrective action.
- 11.4.3 If the Contractor needs to analyze more than the most concentrated extract and two (2) sample dilutions to have all the pesticide/Aroclor compounds within the calibration range of the instrument, contact Sample Management Office (SMO). SMO will contact the Region for instructions.

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- 11.4.4 Sample re-extraction/re-analyses performed as a result of suspected matrix interferences beyond the scope of the method will be reviewed on a case-by-case basis for payment purposes by the USEPA Contract Laboratory Program Project Officer (CLP PO). Send a copy of the SDG Narrative (including your contract number), a description of the situation, and the requested action to the CLP PO.

## 12.0 QUALITY CONTROL

### 12.1 Blank Analyses

#### 12.1.1 Introduction

There are two types of blanks required by this method: the method blank and the instrument blank. A separate sulfur cleanup blank may also be required if some, but not all of the samples are subjected to sulfur cleanup. Samples that are associated with a sulfur cleanup blank are also associated with the method blank with which they were extracted. Both the method and sulfur cleanup blanks must meet the respective technical acceptance criteria for the sample analysis technical acceptance criteria to be met.

#### 12.1.2 Method Blank

##### 12.1.2.1 Summary of Method Blank

A method blank is 1.0 liter of reagent water carried through the entire analytical scheme. The purpose of a method blank is to determine the levels of contamination associated with the processing and analysis of samples.

##### 12.1.2.2 Frequency of Method Blank

A method blank must be extracted each time samples are extracted. The number of samples extracted with each method blank shall not exceed 20 field samples (excluding matrix spike/matrix spike duplicate, PE samples, and Laboratory Control Samples). In addition, a method blank shall:

- Be extracted by the same procedure used to extract samples; and
- Be analyzed on each Gas Chromatograph/Electron Capture (GC/ECD) system used to analyze associated samples.

##### 12.1.2.3 Procedure for Method Blank

Measure 1.0 liter of reagent water for each method blank aliquot. Add 200 µL of the surrogate solution (Section 7.2.3.1). Extract, concentrate and analyze the method blank according to Section 10.

##### 12.1.2.4 Calculations for Method Blank

Calculate method blank results according to Section 11.

##### 12.1.2.5 Technical Acceptance Criteria for Method Blank

12.1.2.5.1 The requirements below apply independently to each GC column and to all instruments used for these analyses. Quantitation must be performed on each GC column.

12.1.2.5.2 All method blanks must be prepared and analyzed at the frequency described in Section 12.1.2.2, using the procedure in Section 12.1.2.3 on a GC/ECD system meeting the initial calibration and calibration verification technical acceptance criteria. Method blanks must be cleaned-up using Florisil meeting the technical acceptance criteria for florisil.

12.1.2.5.3 Method blanks must be bracketed at 12-hour intervals (or less) by acceptable analyses of instrument blanks, PEMs, and

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- individual Standard Mixtures A and B as described in Section 10.2.2.1.
- 12.1.2.5.4 The concentration of the target compounds (Exhibit C - Pesticides) in the method blank must be less than the Contract Required Quantitation Limit (CRQL) for each target compound.
- 12.1.2.5.5 The method blank must meet all sample technical acceptance criteria in Sections 11.3.5 to 11.3.9.
- 12.1.2.5.6 Surrogate recoveries must fall within the acceptance window of 30-150 percent. These limits are not advisory.
- 12.1.2.6 Corrective Action for Method Blank
- 12.1.2.6.1 If a method blank does not meet the technical acceptance criteria the Contractor must consider the analytical system to be out of control.
- 12.1.2.6.2 If contamination is a problem, the source of the contamination must be investigated and appropriate corrective measures MUST be taken and documented before further sample analysis proceeds. Further, all samples (including Laboratory Control Samples, requested matrix spike/matrix spike duplicate, and PE samples) processed with a method blank that does not meet the method blank technical acceptance criteria (i.e., contaminated) will require re-extraction and re-analysis at no additional cost to USEPA. It is the Contractor's responsibility to ensure that method interferences caused by contaminants in solvents, reagents, glassware, and sample storage and processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms be eliminated.
- 12.1.2.6.3 If surrogate recoveries in the method blank do not meet the technical acceptance criteria, listed in 12.1.2.5.6, first re-analyze the method blank. If the surrogate recoveries do not meet the technical acceptance criteria after re-analysis, then the method blank and all samples (including Laboratory Control Samples, requested matrix spike/matrix spike duplicate, and PE samples) associated with that method blank must be re-extracted and re-analyzed at no additional cost to USEPA.
- 12.1.2.6.4 If the method blank fails to meet a technical acceptance criteria other than Sections 12.1.2.5.4 and 12.1.2.5.6, then the problem is an instrument problem. Correct the instrument problem, recalibrate the instrument (if necessary) and re-analyze the method blank.
- 12.1.3 Sulfur Cleanup Blank
- 12.1.3.1 Summary of Sulfur Cleanup Blank
- The sulfur cleanup blank is a modified form of the method blank. The sulfur cleanup blank is hexane spiked with the surrogates and passed through the sulfur cleanup and analysis procedures. The purpose of the sulfur cleanup is to determine the levels of contamination associated with the separate sulfur cleanup steps.
- 12.1.3.2 Frequency of Sulfur Cleanup Blank
- The sulfur cleanup blank is prepared when only part of a set of samples extracted together requires sulfur removal. A method blank is associated with the entire set of samples. The sulfur

cleanup blank is associated with the part of the set which required sulfur cleanup. If all the samples associated with a given method blank are subjected to sulfur cleanup, then no separate sulfur cleanup blank is required.

12.1.3.3 Procedure for Sulfur Cleanup Blank

The concentrated volume of the blank must be the same as the final volume of the samples associated with the blank. The sulfur blank must also contain the surrogates at the same concentrations as the sample extracts (assuming 100.0 percent recovery). Therefore, add 0.2 milliliters (mL) of the surrogate spiking solution (Section 7.2.3.1) to 1.8 mL of hexane in a clean vial.

12.1.3.3.2 Proceed with the sulfur removal (Section 10.1.5.3) using the same technique (mercury or copper) as the samples associated with the blank.

12.1.3.3.3 Analyze the sulfur blank according to Section 10.2.

12.1.3.4 Calculations for Sulfur Cleanup Blank

12.1.3.4.1 Assuming that the material in the sulfur blank resulted from the extraction of a 1 L water sample, calculate the concentration of each analyte using Equation 12 in Section 11.2.1.8. Compare the results to the CRQL values in Exhibit C (Pesticides).

12.1.3.4.2 See Section 11.2 for the equations for the other calculations.

12.1.3.5 Technical Acceptance Criteria for Sulfur Cleanup Blanks

12.1.3.5.1 The requirements below apply independently to each GC column and to all instruments used for these analyses. Quantitation must be performed on each column.

12.1.3.5.2 All sulfur cleanup blanks must be prepared and analyzed at the frequency described in Section 12.1.3.2 using the procedure in Section 12.1.3.3 on a GC/ECD system meeting the initial calibration and calibration verification technical acceptance criteria.

12.1.3.5.3 Sulfur cleanup blanks must be bracketed at 12-hour intervals (or less) by acceptable analyses of instrument blanks, PEMs and Individual Standard Mixtures A and B, as described in Section 10.2.2.1.

12.1.3.5.4 The concentration of the target compounds (Exhibit C - Pesticides) in the sulfur cleanup blank must be less than the CRQL for each target compound.

12.1.3.5.5 The sulfur cleanup blank must meet all sample technical acceptance criteria in Sections 11.3.5 to 11.3.9.

12.1.3.5.6 Surrogate recoveries must fall within the acceptance windows of 30-150 percent.

12.1.3.6 Corrective Action for Sulfur Cleanup Blank

12.1.3.6.1 If a sulfur cleanup blank does not meet the technical acceptance criteria, the Contractor must consider the analytical system to be out of control.



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- 12.1.3.6.2        If contamination is a problem, the source of the contamination must be investigated and appropriate corrective measures MUST be taken and documented before further sample analysis proceeds. Further, all samples processed with a sulfur cleanup blank that does not meet the sulfur cleanup blank technical acceptance criteria (i.e., contaminated) will require re-extraction and re-analysis at no additional cost to USEPA. It is the Contractor's responsibility to ensure that method interferences caused by contaminants in solvents, reagents, glassware, and sample storage and processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms be eliminated.
- 12.1.3.6.3        If surrogate recoveries in the sulfur cleanup blank do not meet the technical acceptance criteria, in Section 12.1.3.5.6, first re-analyze the sulfur cleanup blank. If the surrogate recoveries do not meet the technical acceptance criteria after re-analysis, then the sulfur cleanup blank and all samples associated with that sulfur cleanup blank must be re-prepared/re-extracted and re-analyzed at no additional cost to USEPA.
- 12.1.3.6.4        If the sulfur cleanup blank fails to meet a technical acceptance criteria other than Sections 12.1.3.5.4, and 12.1.3.5.6, then the problem is an instrument problem. Correct the instrument problem, recalibrate the instrument (if necessary) and re-analyze the sulfur cleanup blank.
- 12.1.4        Instrument Blank
- 12.1.4.1        Summary of Instrument Blank
- An instrument blank is a volume of clean solvent spiked with the surrogates and analyzed on each GC column and instrument used for sample analysis. The purpose of the instrument blank is to determine the levels of contamination associated with the instrumental analysis particularly with regard to carryover of analytes from standards or highly contaminated samples into other analysis.
- 12.1.4.2        Frequency of Instrument Blank
- The first analysis in a 12-hour analysis sequence (Section 9.3.2) must be an instrument blank. All groups of acceptable sample analyses are to be preceded and followed by acceptable instrument blanks (Section 10.2.2.1). If more than 12 hours have elapsed since the injection of the instrument blank that bracketed a previous 12-hour period, an instrument blank must be analyzed to initiate a new 12-hour sequence (Section 9.3.2).
- 12.1.4.3        Procedure for Instrument Blank
- 12.1.4.3.1        Prepare the instrument blank by spiking the surrogates into hexane or iso-octane for a concentration of 20.0 nanograms per milliliter (ng/mL) of Tetrachloro-m-xylene and Decachlorobiphenyl.
- 12.1.4.3.2        Analyze the instrument blank according to Section 10.2 at the frequency listed in Section 12.1.4.2.

12.1.4.4 Calculations for Instrument Blank

12.1.4.4.1 Assuming that the material in the instrument blank resulted from the extraction of a 1 L water sample, calculate the concentration of each analyte using Equation 12 in Section 11.2.1.8. Compare the results to the CRQL values for water samples in Exhibit C (Pesticides).

12.1.4.4.2 See Section 11.2 for the equations for the other calculations.

12.1.4.5 Technical Acceptance Criteria for Instrument Blanks

12.1.4.5.1 The requirements below apply independently to each GC column and to all instruments used for these analyses. Quantitation must be performed on each GC column.

12.1.4.5.2 All instrument blanks must be prepared and analyzed at the frequency described in Section 12.1.4.2 using the procedure in Section 10.2 on a GC/ECD system meeting the initial calibration and calibration verification technical acceptance criteria.

12.1.4.5.3 The concentration of each target analyte (Exhibit C - Pesticides) in the instrument blank must be less than the CRQL for that analyte.

12.1.4.5.4 The instrument blank must meet all sample technical acceptance criteria in Sections 11.3.5 to 11.3.9.

12.1.4.6 Corrective Action for Instrument Blank

12.1.4.6.1 If analytes are detected at concentrations greater than the CRQL or the surrogate Retention Times (RTs) are outside the RT windows, all data collection must be stopped, and corrective action must be taken. Data for samples which were run between the last acceptable instrument blank and the unacceptable blank are considered suspect. An acceptable instrument blank must be run before additional data are collected. All samples (including Laboratory Control Samples, requested matrix spike/matrix spike duplicate, and PE samples) and required blanks which were run after the last acceptable instrument blank must be reinjected during a valid run sequence and must be reported at no additional cost to USEPA.

12.2 Laboratory Control Sample (LCS)

12.2.1 Summary of LCS

The LCS is an internal laboratory quality control sample designed to assess [on a Sample Delivery Group (SDG)-by-SDG basis] the capability of the contractor to perform the analytical method listed in this Exhibit.

12.2.2 Frequency of LCS

The LCS must be prepared, extracted, analyzed, and reported once per Sample Delivery Group. The LCS must be extracted and analyzed concurrently with the samples in the SDG using the same extraction protocol and instrumentation as the samples in the SDG.

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12.2.3 Procedure for LCS

Measure a 1 liter aliquot of reagent water in a 1 liter graduated cylinder and transfer the water to a continuous extractor or 2 L separatory funnel. Pipet 1.0 mL of the LCS spiking solution (Section 7.2.3.8) and 200 uL of the surrogate standard spiking solution into the water and mix well. Extract, concentrate, and analyze the sample according to Section 10.

12.2.4 Calculations for LCS

12.2.4.1 Calculate the results according to Section 11.

12.2.4.2 Calculate individual compound recoveries of the LCS using Equation 15.

12.2.5 Technical Acceptance Criteria For LCS

12.2.5.1 The requirements below apply independently to each GC column and to all instruments used for these analyses. Quantitation must be performed on each GC column.

12.2.5.2 The LCS must be analyzed at the frequency described in Section 12.2.2 on a GC/ECD system meeting the initial calibration and calibration verification technical acceptance criteria.

12.2.5.3 The LCS must be prepared as described in Section 12.2.3.

12.2.5.4 The LCS must meet all sample technical acceptance criteria in Sections 11.3.5 to 11.3.9.

12.2.5.5 The percent recovery for each of the compounds in the LCS must be within the recovery limits listed in Table D-3.

12.2.6 Corrective Action for LCS

12.2.6.1 If the LCS technical acceptance criteria for the surrogates or the LCS compound recovery are not met, check calculations, the surrogate and LCS solutions, and instrument performance. It may be necessary to recalibrate the instrument or take other corrective action procedures to meet the surrogate and LCS recovery criteria.

12.2.6.2 LCS technical acceptance criteria MUST be met before data are reported. LCS contamination from laboratory sources or any LCS analyzed not meeting the technical acceptance criteria will require re-extraction and re-analysis of the LCS at no additional cost to USEPA.

12.2.6.3 All samples (including matrix spike/matrix spike duplicate and PE samples) and required blanks, prepared and analyzed in an SDG with an LCS that does not meet the technical acceptance criteria, will also require re-extraction and re-analysis at no additional cost to USEPA.

12.3 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

12.3.1 Summary of MS/MSD

In order to evaluate the effects of the sample matrix on the methods used for pesticide/Aroclor analyses, USEPA has prescribed a mixture of pesticide/Aroclor target compounds to be spiked into two aliquots of a sample, and analyzed in accordance with the appropriate method.

12.3.2 Frequency of MS/MSD Analysis

- 12.3.2.1 MS/MSD samples shall only be analyzed if requested by the Region [through Sample Management Office (SMO)] or specified on the Traffic Report (TR). If requested, a matrix spike and matrix spike duplicate must be extracted and analyzed for every 20 field samples in an SDG.
- 12.3.2.2 As part of USEPA's QA/QC program, water rinsate samples and/or field blanks may be delivered to a laboratory for analysis. Do not perform MS/MSD analysis on a water rinsate sample or field blank.
- 12.3.2.3 If the USEPA Region requesting MS/MSD designates a sample to be used as an MS/MSD, then that sample must be used. If there is insufficient sample volume remaining to perform an MS/MSD, then the Contractor shall choose another sample to perform an MS/MSD analysis. At the time the selection is made, the Contractor shall notify the Region (through SMO) that insufficient sample was received and identify the USEPA sample selected for the MS/MSD analysis. The rationale for the choice of another sample other than the one designated by USEPA shall be documented in the SDG Narrative.
- 12.3.2.4 If there is insufficient sample volume remaining in any of the samples in an SDG to perform the requested MS/MSD, the Contractor shall immediately contact SMO to inform them of the problem. SMO will contact the Region for instructions. The Region will either approve that no MS/MSD be performed, or require that a reduced sample aliquot be used for the MS/MSD analysis. SMO will notify the Contractor of the Region's decision. The Contractor shall document the decision in the SDG Narrative.
- 12.3.2.5 If it appears that the Region has requested MS/MSD analysis at a greater frequency than specified in Section 12.3.2.1, the Contractor shall contact SMO. SMO will contact the Region to determine which samples should have MS/MSD performed on them. SMO will notify the Contractor of the Region's decision. The Contractor shall document the decision in the SDG Narrative. If this procedure is not followed, the Contractor will not be paid for MS/MSD analysis performed at a greater frequency than required by the contract.
- 12.3.2.6 When a Contractor receives only Performance Evaluation (PE) samples, no MS/MSD shall be performed within that SDG.
- 12.3.2.7 When a Contractor receives a PE sample as part of a larger SDG, a sample other than the PE sample must be chosen for the requested MS/MSD analysis when the Region did not designate a sample to be used for this purpose.

12.3.3 Procedure for Preparing MS/MSD

- 12.3.3.1 Measure out two additional 1 L aliquots of the sample chosen for spiking. Adjust the pH of the samples (if required) and fortify each with 1 mL of the matrix spiking solution (Section 7.2.3.2). Using a syringe or volumetric pipet, add 200 uL of the surrogate spiking solution (Section 7.2.3.1) to each sample. Extract, concentrate, cleanup, and analyze the matrix spike and matrix spike duplicate according to Section 10.0.
- 12.3.3.2 Matrix spike and matrix spike duplicate samples must be analyzed at the same concentration as the most concentrated extract for

which the original sample results will be reported. Do not further dilute the MS/MSD samples to get either spiked or nonspiked analytes within calibration range.

#### 12.3.4 Calculations for MS/MSD

The percent recoveries and the relative percent difference between the recoveries of each of the compounds in the matrix spike and matrix spike duplicate samples will be calculated and reported by using the following equations:

EQ. 16

$$\text{Matrix Spike Recovery} = \frac{\text{SSR} - \text{SR}}{\text{SA}} \times 100$$

Where:

SSR = Spike sample result.  
SR = Sample result.  
SA = Spike added.

EQ. 17

$$\text{RPD} = \frac{|\text{MSR} - \text{MSDR}|}{\frac{1}{2} (\text{MSR} + \text{MSDR})} \times 100$$

Where:

RPD = Relative percent difference.  
MSR = Matrix spike recovery.  
MSDR = Matrix spike duplicate recovery.

#### 12.3.5 Technical Acceptance Criteria for MS/MSD

- 12.3.5.1 The requirements below apply independently to each GC column and to all instruments used for these analyses. Quantitation must be performed on each GC column.
- 12.3.5.2 If requested, all MS/MSD must be prepared and analyzed at the frequency described in Section 12.3.2, using the procedure above and in Section 10 on a GC/ECD system meeting the initial calibration, calibration verification, and blank technical acceptance criteria. MS/MSD must be cleaned-up using florisil meeting the technical acceptance criteria for florisil. MS/MSD must be bracketed at 12-hour intervals (or less) by acceptable analyses of instrument blanks, PEMs, and individual standard mixtures A and B as described in Section 10.2.2.1.
- 12.3.5.3 The samples must be extracted and analyzed within the contract required holding times.
- 12.3.5.4 The RT for each of the surrogates must be within the RT window as calculated in Section 9 for both GC columns.

12.3.5.5 The limits for matrix spike compound recovery and RPD are given in Table D-4. As these limits are only advisory, no further action by the laboratory is required. However, frequent failures to meet the limits for recovery or RPD warrant investigation by the laboratory, and may result in questions from USEPA.

12.3.6 Corrective Action for MS/MSD

Any MS/MSD which fails to meet the technical acceptance criteria in Sections 12.3.5.1 through 12.3.5.4 must be re-analyzed at no additional cost to USEPA.

12.4 Method Detection Limit (MDL) Determination

12.4.1 Before any field samples are analyzed under this contract, the MDL for each pesticide target compound shall be determined for each sample extraction procedure and on one of the instruments to be used for sample analysis. The MDLs must be verified annually thereafter (see Section 12.4.2 for MDL verification procedures), until the contract expires or is terminated or after major instrument maintenance. Major instrument maintenance includes, but is not limited to replacement of gas chromatographic column or replacement of the electron capture detector.

12.4.2 To determine the MDLs, the Contractor shall run an MDL study following the procedures specified in 40 CFR Part 136. The Contractor is only required to analyze the MDL samples on one instrument used for field sample analyses. MDL verification only is then required on all other instruments used for field sample analysis and at the frequency specified in Section 12.4.1. MDL verification is achieved by analyzing a single reagent water blank spiked with each target compound at a concentration equal to two times the analytical determined MDL. The resulting chromatogram must meet the qualitative identification criteria outlined in Sections 11.1.1 through 11.1.5.

12.4.3 The determined concentration of the MDL must be less than the CRQL.

12.4.4 All documentation for the MDL studies shall be maintained at the laboratory and provided to USEPA upon written request.

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Method Performance

13.0 METHOD PERFORMANCE

Not Applicable.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The USEPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, USEPA recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions, consult *Less is Better: Laboratory Chemical Management for Waste Reduction*, available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington, D.C. 20036, (202)872-4477.

15.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. USEPA urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management consult *The Waste Management Manual for Laboratory Personnel*, available from the American Chemical Society at the address listed in Section 14.2.

16.0 REFERENCES

Not Applicable.

17.0 TABLES/DIAGRAMS/FLOWCHARTS

TABLE D-1

RETENTION TIME WINDOWS FOR SINGLE AND MULTICOMPONENT  
ANALYTES AND SURROGATES.

Compound	Compound Identification Window (minutes)
alpha-BHC	±0.05
beta-BHC	±0.05
gamma-BHC	±0.05
delta-BHC	±0.05
Heptachlor	±0.05
Aldrin	±0.05
alpha-Chlordane	±0.07
gamma-Chlordane	±0.07
Heptachlor epoxide	±0.07
Dieldrin	±0.07
Endrin	±0.07
Endrin aldehyde	±0.07
Endrin ketone	±0.07
4,4'-DDD	±0.07
4,4'-DDE	±0.07
4,4'-DDT	±0.07
Endosulfan I	±0.07
Endosulfan II	±0.07
Endosulfan sulfate	±0.07
Methoxychlor	±0.07
Aroclors	±0.07
Toxaphene	±0.07
Tetrachloro-m-xylene	±0.05
Decachlorobiphenyl	±0.10



TABLE D-2  
NUMBER OF POTENTIAL QUANTITATION PEAKS

Multicomponent Analyte	No. of Potential Quantitation Peaks
Aroclor 1016/1260	5/5
Aroclor 1221	3
Aroclor 1232	4
Aroclor 1242	5
Aroclor 1248	5
Aroclor 1254	5
Toxaphene	4

TABLE D-3

LABORATORY CONTROL SAMPLE RECOVERY LIMITS

Compound	% Recovery
gamma-BHC	50-120
Heptachlor epoxide	50-150
Dieldrin	30-130
4,4'-DDE	50-150
Endrin	50-120
Endosulfan sulfate	50-120
gamma-Chlordane	30-130

NOTE: The recovery limits for any of the compounds in the LCS may be expanded at any time during the period of performance if USEPA determines that the limits are too restrictive.

TABLE D-4

MATRIX SPIKE RECOVERY AND RELATIVE PERCENT DIFFERENCE LIMITS

Compound	% Recovery	RPD
gamma-BHC (Lindane)	56-123	15
Heptachlor	40-131	20
Aldrin	40-120	22
Dieldrin	52-126	18
Endrin	56-121	21
4,4'-DDT	38-127	27